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«High-Tech in Chemical Engineering – 2016»
with elements of school of young scientists

ABSTRACTS

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Scientific Program of the Conference

- Plenary Lectures (40 min)
- Oral Reports (up to 20 min)
- Poster Session

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Plenary Lectures
UDC 544.015.34:66.011

PHASE BEHAVIOUR OF MULTICOMPONENT FLUID MIXTURES OF ORGANIC COMPOUNDS: PREDICTION AND ANALYSIS OF PROPERTIES, STRUCTURE OF PHASE DIAGRAM, DEVELOPMENT OF ENERGY EFFECTIVE SEPARATION FLOWSHEET

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The fundamental connection of phase diagrams of liquid-vapor equilibrium and liquid-liquid equilibrium with the structure of flowsheet of fluid mixtures separation and columns operating parameters is the basis for solving problems related to development of energy efficient technologies of organic compounds production.

Identification of the general laws of formation of structures of phase diagrams of multicomponent multiphase systems, slightly presented in foreign and domestic literature; prediction of their phase behavior, including homologous systems; development of elements of thermodynamic-geometric analysis of diagrams of splitting systems; synthesis of the separation flowsheet based on the combination of rectification and splitting process are actual problems. Studies in these areas are actively being developed in the framework of the scientific school of Professor L.A. Serafimov and they make a significant contribution to the development of thermodynamics of heterogeneous systems and theoretical foundations of processes of heteroazeotropic mixtures separation.

A method of prediction of the presence / absence of four- and five-component azeotrope, based on the analysis of topological characteristics of singular points and signs of the characteristic roots of the system of linear approximation of the distillation process was proposed and was tested on systems of different physical-chemical nature. In the system acetone – chloroform – ethanol – cyclohexane – water the existence of five-component azeotrope was predicted.

Approaches and algorithms to study the evolution of the splitting areas in the concentration tetrahedron of the systems isoprene – trimethylene – acetonitrile – water, cyclohexanone – cyclohexene – acetonitrile – water were developed.

The perspectivity of the use of homologous systems (for example, ternary systems acetone – alcohol C1- C5 – saturated hydrocarbons C6- C10; aniline – water – saturated hydrocarbon C6-C10) for predicting azeotropy, presence and size of splitting areas with different number of liquid phases was shown.

The influence of mutual location of three- and two-phase immiscibility and separatrices manifolds on the structure of flowsheet, columns static parameters, the energy consumption for separation was shown on the basis of thermodynamic-geometric analysis of phase diagrams of model and real four-component systems (isoprene – trimethylene-acetonitrile – water, alkanes C6-C8 – cyclohexane – furfural –water).

The study of phase equilibrium, general laws of phase diagrams formation, development of separation flowsheets on this basis is a sustainable area of new knowledge and its applications for development of engineering companies and the industry as a whole.
Membrane gas separation is an efficient, environmentally friendly process, well developed for nitrogen and oxygen production from air. The search for new membrane materials with high permeability and selectivity for different gas pairs is an important goal in membrane material science.

We have developed a methodology of the synthesis and have created new highly permeable materials for gas separation membranes based on silyl substituted norbornenes (NBs) and their analogues – tricyclononenes (TCNs) [1]. The methodology includes a simple synthesis of norbornene-type monomers and their polymerization according to schemes of metathesis (MP) and addition (vinyl) (AP) polymerizations with obtaining polymers of different main chain structures.

This methodology gave us an opportunity to obtain a great number of polymers with the regularly variable structures and to find out some new relationships between polymers structure and their gas permeability. This led to the discovery of a new class of highly permeable glassy polymers – addition silicon-substituted polynorbornenes and polytricyclononenes (APNB) belonging to a small group of very high permeable glassy polymers (P(O2) up to 2400 Barrer) with large free volume. The rigid polymer chain and the bulky Me3Si-substituents are responsible for the formation of the large free volume in APNB. Metathesis polynorbornenes (MPNB) possessing less rigid polymer backbone have lower permeability than the APNB. An important and interesting feature of all the APNB as well as MPNB with Si–O–Si-containing substituents is their ability to separate hydrocarbon gases C3+ from C1, which is typical for rubber and is extremely rare for glassy polymers. Good thermal and chemical stability allow including the APNB into the family of most promising materials for membrane application.

Reference:
DRIFT SPECTROMETRY: TRADITIONAL METHODS AND THEIR DEVELOPMENT PROSPECTS

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A brief review of the traditional drift-spectrometry methods has been given: time-of-flight ionic mobility spectrometry, ionic mobility incrementation spectrometry, tandem drift-spectrometry of various modifications. Well-known information on surface-ionization drift-spectrometry has been presented from the related papers, and main trends of development of this method having a number of advantages over the available ones have been formulated.

BIOANALYTICAL AND IMAGING REAGENTS BASED ON POLYACROLEIN MICROSPHERES

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Manufacturing techniques of microsphere dispersions on the basis of polyacrolein filled with organic dyes, luminescent inorganic nanocrystals excited by light from ultraviolet or infrared spectral ranges are considered. The microspheres of obtained dispersions are used as bioligand carriers in immunochemical assays with visual and instrumental detection, as cell receptor markers, as imaging agents for in vivo analysis. Preparation of polyacrolein containing microspheres with pH- and thermosensitive fluorescence and their use in bioassays are discussed.
ABOUT THE INDUSTRY OF ADHESIVES AND SEALANTS IN RUSSIA

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Использование клеящих веществ человеком для повседневных нужд началось с незапамятных времен, такое утверждение относится и к герметизирующим материалам – человек столкнулся с необходимостью защиты своего жилья от внешних факторов еще со времен Адама и Евы.

Первые фабрики по производству клеев появились в Европе еще в 17 веке это были клеи природного происхождения или на основе протеинов, получаемые путем кипячения в воде кожи и костей животных. Объемы их производства и потребности в энергии для производства клея были настолько малы, что они не могли оказать какое-либо влияние на экосистему Земли.

Все это коренным образом изменилось в связи с индустриализацией человеческого общества. Сегодня в мире производится и потребляется более 12 млн. тонн клеев и герметиков, в том числе, до 0,5 млн тонн в России.

Быстрый рост населения Земли в 20-м столетии, резкое увеличение потребления товаров и услуг имели драматические последствия для экологии Земли в целом. Многие товары стали производиться при помощи клеев с высокими потребительскими характеристиками, их потребление особенно возросло после 2-й Мировой войны с связи с успехами в области производства новых специальных полимеров и создания химически отверждаемых клеев и клеев-расплавов. В будущем новые поколения современных клеев и клеев-герметиков позволят создать еще больше новых товаров и изделий с выдающимися потребительскими характеристиками.

Несколько декад тому назад за рубежом была предложена идея «устойчивого» развития ("sustainability, sustainable"), подразумевая под этим емким выражением уменьшение вклада результатов человеческой деятельности на экосистему Земли до некритических уровней, производство необходимых продуктов, товаров меньшими затратами невозобновляемых сырьевых ресурсов и меньшими энергетическими затратами и др. Индустрия клеев и герметиков развитых стран активно включилась в дискуссию и стала реализовать эту идею на практике (начало исключения из практики клеев на основе органических растворителей, фталатов и др.)

В докладе кроме исторической справки развития производства и потребления клеев и герметиков в мире с древнейших времен до сегодняшних дней и данных исследования рынка клеев и герметиков в мире и России, приводятся некоторые соображения по «устойчивому» развитию индустрии клеев и герметиков.
DEVELOPMENT OF INNOVATIVE TECHNOLOGY FOR CROPS PROTECTANTS
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At the present stage of plant protection should be considered as a prospective direction to minimize the impact of biotic stressors and the optimizing regulatory capacity of agricultural technologies, which negate the environmental and economic risks and promote sustainable agriculture. In this respect, to protect seeds is one of the most environmentally friendly ways of pesticide use and therefore in all developed countries of the world the protecting of seeds refers to the law of mandatory phytosanitary measures directed against a complex of pathogens of crops, transmitted by seeds and remaining in the soil.

It is obvious that the efficacy of pesticides is not only dependent on the nature of the active substance (AS) and its activity, but also the correct choice of formulation AS retaining beneficial properties, the stability of working solutions providing quality of the application and adherence to the treated surface. Development of the formulation takes place on the basis of the adaptation of common methodological principles of nanomaterials research methods, technical means and nanotechnology. And we should expect that these techniques and technologies will improve formulations of pesticides on three main criteria - effectiveness, efficiency and environmental friendliness to the environment.

It is known that most biologically active substances, in particular of pesticides’ AS, belong to the class or bad-insoluble and physiologically active media, which involves excessive use dosages AS and thereby leads to higher drug price and increases its toxicity to the environment. In this regard, our research on the development of innovative medicines based on mechano-chemical methods of modification of the physico-chemical and biological properties of wellknown pesticides, are very popular and relevant. The essence of the approach developed by us is to provide preparations in the form of solid dispersions of pesticides and watersoluble polymers by their joint mechanochemical treatment in a controlled energy input mills. Using the method of mechanochemical modifications refers to regulate properties of pesticides and take the compositions with high water solubility, which suggests an increase in biological activity of the compositions.

In this paper the results of research will be given to the creation of innovative seed treatment of cereals. For example, it was noted a positive effect on almost all indicators of the structure of productivity of grain crops, which ultimately impact on increasing grain yield. It was shown that integrated seed protectants offered by us have a complex effect, namely, exhibit the properties of a fungicide, a plant growth regulator and herbicide antidote residues in the soil. The results indicate the prospects of further studies to optimize the formulation methods of protectants by Mechanochemistry.

Acknowledgements
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Peptide nucleic acids (PNAs) [1] are non-hydrolyzable functional analogues of oligodeoxyribonucleotides (ODNs), which recognize complementary nucleic acid sequences. The synthesis of modified PNAs that are capable of more efficient (affine and selective) binding with ODN targets due to the preorganization of the pseudopeptide backbone conditioned by chiral centers or cyclic fragments [2] is currently the subject of extensive studies. Functional groups of the side residues in acyclic PNA modifications impart additional favourable properties to PNA oligomers.

The main objective of our study was to develop a synthetic strategy and scientific technological background for obtaining polyanionic α- and γ-PNAs based on L-Glu (Fig. 1). Such modified PNAs are preorganized and functionally close to native ONs. They demonstrate improved solubility and can be complexed with cationic transfectants for efficient intracellular delivery.

Monomers (II) were obtained from the respective α- and γ-pseudopeptide precursors (I) and protected heterocyclic bases. The key step of the monomer synthesis was regioselective alkylation of the N1 position of pyrimidine bases or the N9- position of purine bases (the regioselectivity was confirmed by 2D-NMR data). The preparation PNA oligomers (III) required optimization of known protocol [3]. The trisopropylsilane-based systems with strict control of time and temperature were used for PNA removal from the support to avoid degradation of the polyanionic PNA sequences. The introduction of additional N- or C-terminal glycine residues into the oligomer structure was shown to increase the yields of both α- and γ-PNA oligomers by preventing the undesired rearrangements. The following oligomers were obtained: α-H-T10-NH2, γ-H-T10-NH2, H-Gly- α-CAGACTTA-NH2 and H-Gly- γ-CAGACTTA-Gly-NH2. Investigation of their hybridization properties revealed that α-oligomers derived from L-Glu are incapable of forming stable complexes with complementary ODNs, while the respective γ-isomers formed different types of complexes: triplexes (in the case of the homothymine decamer) or stable duplexes (in the case of H-Gly- γ-CAGACTTA-Gly-NH2), both parallel and antiparallel. The latter were thermodynamically more stable than the parallel duplexes (approximately by 10°C).

References:
Органическая химия с момента зарождения и до настоящего времени занимается решением задач, которые делают этот мир таким, каким мы его видим сегодня. Красители, синтетические ткани, все многообразие полимеров, лекарства, специальные материалы и пр, все это органические вещества, без которых не поехал бы ни один автомобиль и не заработал бы ни один компьютер.

Удивительно, но несмотря на самый передовой характер задач органической химии, методы их решения за последние десятилетия поменялись очень незначительно. В этом смысле химики-технологи ушли существенно дальше. Арсенал методов и набор инструментов в их руках, как это ни странно, существенно больше. Технологи придумали и широко используют непрерывные процессы, и только по прошествии полувека микрореакторное оборудование стало появляться в лабораториях. В 1940-х годах в рамках ядерных проектов для разделения практически идентичных по свойствам изотопов урана технологии разработали центрифуги и непрерывную противоточную экстракцию. Но до сих пор экстракция, как метод разделения веществ, не знакома фактически ни одному из ведущих профессоров в области органической химии. Что может дать экстракция и как устранить ограничения в использовании этого метода?

Непрерывная противоточная жидкостная экстракция – в первую очередь метод разделения близких по свойствам веществ, который основан на различном распределении разделяемых веществ в двух несмешивающихся жидкостях. Как правило, в роли первой жидкости выступает вода или водный раствор, а в роли второй – органический растворитель. С этой точки зрения экстракция является аналогом хроматографии, только в роли сорбента выступает жидкость.

Переход от твердой “неподвижной” фазы к подвижной жидкой приводит к тому, что ввод вещества для разделения может быть не только периодическим, но и непрерывным. За счет этого экстракция является существенно более производительным методом, чем хроматография.

Вторым отличием экстракции от хроматографии является возможность разделения полярных соединений, таких как аминокислоты, соли органических и элементоорганических кислот, ионые жидкости и т.п.. Главным отличием экстракции от хроматографии является возможность проведения некоторых реакций, например, реакций обмена, непосредственно в экстракционной установке.

В докладе рассмотрены особенности конструкций современных экстракторов и примеры задач, которые могут быть легко решены с использованием непрерывной противоточной экстракции.
Due to the rapid development of genetic engineering, modern biotechnology, which has its origins in the early eighties of the last century, allows to insert foreign genes into bacterial cells and to obtain biologically active molecules, mainly for medical practice applications. Obviously, special attention was paid primarily to hormones such as insulin, human growth hormone, other hormones that were isolated from animal raw material, but their chemical structure was not identical to that of the human body hormones. However, it should be recognized that elements of biotechnology were used previously as well, for example, in the production of semisynthetic beta-lactam antibiotics (penicillins and cephalosporins). Due to the studies on the determination of the human genome, as well as advances in the field of proteomics, it became clear that methods of genetic engineering allow to obtain not only individual molecules of biopolymers, but the whole systems, such as, for example, receptors of biologically active molecules, ion channels, various types of enzymes. The availability of this kind of biological targets not only allows determining their spatial structure by various physicochemical methods, but also opens opportunities for the design of novel pharmaceuticals by chemical and biotechnological methods.

The ambitious program for the next decade involving full synthesis of the human genome, obviously, can be realized only by cooperation of chemical and biotechnological approaches. Creating molecules comprising up to 3.5 billion pairs of nucleotides will become possible only if there are effective methods of synthesizing nucleic acids, both chemical and biotechnological. One can give a number of examples of the production of more active analogues of natural hormones, by their chemical modification or by introduction of unnatural amino acid residues. In case of the technology of peptide and protein drugs production, both chemical and biotechnological mixed methods are also widely used. To obtain peptides consisting of up to 60 amino acid residues chemical synthesis is more convenient, while for larger protein molecules, using genetic engineering techniques is preferable.

The main part of the report is devoted to the development of the biotechnological systems of synthesis of nucleosides and nucleotides, both naturally occurring and modified at the heterocyclic bases and carbohydrate residues. Based on the data of X-ray diffraction analysis of transglycosylation enzymes, amino acid residues of the active site were identified. Their substitution by point mutations results in the altering of the binding specificity with substrates of different chemical structure.
Ряд производных антрацендиона (антрахинона), например антрациклиновые антибиотики (доксорубицин 1), широко используются в современной химиотерапии для лечения онкологических заболеваний. Несмотря на клиническую эффективность этого класса противоопухолевых средств, их использование ограничивается рядом недостатков, важнейшими из которых являются высокая кардиотоксичность и развитие у опухолевых клеток множественной лекарственной устойчивости (МЛУ). Поэтому изыскание более доступных и эффективных противоопухолевых препаратов с улучшенными химиотерапевтическими свойствами является актуальной задачей фармацевтической хими.

Индол и его производные традиционно считаются в медицинской химии «привилегированными структурами». Поэтому, конденсированные системы, в которых антрацендионовый скаффолд аннелирован с индольным или другими гетероциклическими ядрами, несомненно, перспективны для изыскания новых химиотерапевтических средств. Используя «fragment-based» подход для генерации потенциальных соединений-лидеров для поиска потенциальных противоопухолевых агентов был выбран нафтоиндольный аналог триптамина 3 [1]. Последующая оптимизация структуры боковой цепи («hit-to-lead») привела к открытию противоопухолевых аминометильных производных 4 [2]. Модификация структуры скаффолда найденного противоопухолевого лидера 4 («scaffold-hopping») и спейсерной группы, присоединяющей остаток диамина к хромофору, привела к открытию производных антрафуран-3-карбоксамида, обладающих высокой цитотоксической активностью. Заключительная оптимизация структуры диамина и скрининга биологических свойств серии 5,10-диоксоантра[2,3-b]фуран-3-карбоксамидов выявило новое соединение-лидер – антрафурандион 5, способное в субмикромолярных и микромолярных концентрациях индуцировать апоптоз опухолевых клеток. В результате углубленных доклинических исследований антрафуран 5 продемонстрировал высокую противоопухолевую активность, включая модели резистентных опухолей in vivo. Исследования внутриклеточных мишеней выявили мультиаргетный механизм действия антрафурана: он способен ингибировать топоизомеразы 1 и 2, а также ряд протеинкиназ, включая AURKA, AURKB и PIM1 [3].
Армированные пластики широко используются в авиа-космической отрасли, машиностроении, при постройке современной военной техники и др.

На современном этапе развития полимерного материаловедения отсутствует классификация армированных систем с использованием параметров их структуры, что не позволяет проводить комплексные обобщения, оптимизировать технологии получения высокопрочных армированных материалов и изделий с волокнами разной природы и структурной организацией.

Нами впервые предлагается классификация армированных в одном направлении пластиков (1D-пластики) по структурному принципу на основе анализа структурообразования при введении волокнистого армирующего наполнителя в полимерные матрицы и описания структуры в рамках обобщенных параметров (a<sub>cp</sub>/d), учитывающих одновременно диаметр (d), упаковку (φ<sub>m,f</sub>) и содержание волокон (φ<sub>f</sub>).

Классификация АрПКМ по структурному принципу и обобщенному параметру (a<sub>cp</sub>/d) при кубической (или гексагональной) упаковке однонаправленных волокон (φ<sub>m,f</sub>=0,785об. д. или φ<sub>m,f</sub>=0,905об. д.) представлена ниже:

- не армированные - a<sub>cp</sub>/d ≥ 3,0 и φ<sub>f</sub> ≤ 5 об. %;
- слабо армированные - 3,0 ≥ a<sub>cp</sub>/d ≥ 1,0 и 5 ≤ φ<sub>f</sub> ≤ 20 об. %;
- средне армированные - 1,0 ≥ a<sub>cp</sub>/d ≥ 0,5 и 20 ≤ φ<sub>f</sub> ≤ 35 об. %;
- армированные - 0,5 ≥ a<sub>cp</sub>/d ≥ 0,25 и 35 ≤ φ<sub>f</sub> ≤ 50 об. %;
- высоко армированные - 0,25 ≥ a<sub>cp</sub>/d ≥ 0,125 и 50 ≤ φ<sub>f</sub> ≤ 65 об. %;
- предельно армированные - 0,125 ≥ a<sub>cp</sub>/d ≥ 0,0 и 65 ≤ φ<sub>f</sub> ≤ φ<sub>m,f</sub>, об. %;
- сверхвысоко армированные - a<sub>cp</sub>/d < 0,0 и φ<sub>f</sub> > φ<sub>m,f</sub>, об. %.

Предлагаемая классификация охватывает весь диапазон армированных 1D-пластиков по составам.

На практике в основном используются армированные, высоко- и предельно армированные полимерные системы.

Показано, что такая система классификации хорошо отражает многочисленные экспериментальные данные по свойствам АрПКМ, полученных в работах как отечественных, так и зарубежных исследователей.

Рассматриваются характерные свойства АрПКМ в соответствии с их классификацией по группам, а также пропитка волокнистых систем и современные методы их переработки в изделия.

Установлено, что выбор методов переработки армированных пластиков следует осуществлять с учетом, предлагаемого деления АрПКМ по группам, согласно предлагаемой классификации.

Такой подход к конструированию структуры и составов армированных пластиков позволяет проводить более полный анализ их свойств с помощью обобщающих параметров и корректно сравнивать результаты с разными армирующими волокнами и полимерными связующими (матрицами).

Разработаны специальные таблицы для целенаправленной разработки составов армированных пластиков с заданной структурой, обобщенными параметрами и свойствами, что позволяет на стадии их проектирования создавать армированные системы с требуемым комплексом технологических и эксплуатационных свойств.
CATALYTIC THERMOPROCESSING OF PETROLEUM-CONTAINING WASTE


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Petroleum-containing waste can be a valuable source of energy and chemicals. There are different methods of waste processing among which pyrolysis, gasification, combustion [1] and co-pyrolysis [2] are the most investigated. The use of thermal degradation of petroleum residues allows obtaining valuable gaseous and liquid products [3]. The product composition mainly depends on the nature of petroleum waste, reaction conditions and the presence of the catalyst. Catalytic pyrolysis of oil-containing waste is conducted at rather low temperatures (400–700°C) in the presence of natural aluminosilicates [4], zeolites [5] and Ni-Mo-containing catalyst [6]. In this paper we focused on the study of oil-slime pyrolysis products obtained in both non-catalytic and catalytic processes to compare their volubility and calorific value.

The oil sludge feed with calculated amount of the catalyst – iron subgroup metal chlorides - (1-20% (wt.)) were processed in laboratory setup in nitrogen medium at temperature 450-600°C. The duration of the test was an hour and a half and each test was repeated at least 3 times. At the experiment completion the following parameters were determined: solid residue weight according to the change of the reactor weight; liquid fraction weight according to water trap and sampler weight; gas weight according to the difference of the initial sample and liquid and solid residue weight. Standard deviation for the pyrolysis product measurement was ±0.5% (wt.).

The analysis of oil-slime pyrolysis products obtained at the optimal conditions (temperature 500°C, nitrogen medium) in the presence of CoCl₂ showed that the presence of catalyst:
- increases total calorific value of gaseous products by 2.2 times compared to non-catalytic process due to the increase in low-weight hydrocarbon content;
- increases the calorific value of liquid products compared to non-catalytic process due to the increase in the amount of cyclic, aromatic and high-weight branched hydrocarbons.

Thus the use of CoCl₂ as the catalyst for the pyrolysis allows effectively processing oil-containing residue with the formation of valuable gaseous and liquid products with high heat of combustion. Moreover the analysis of pyrolysis solid residue showed that the catalyst fully remained in mineral fraction which is represented by graphite-coated silica and can be used as a porous sorbent.

References:
Organometallic vapor phase epitaxy (OMVPE) is a well-established technique for growing semiconductor heterostructures with precision and details at the nanoscale. It is distinguished from other epitaxy methods by its use of organometallic compounds as precursors, which brings about different and rich processes during the evolution of the crystalline surfaces and interfaces. In particular, this epitaxy method is useful for constructing three-dimensional (3D) nanostructures with applications in nano-electronics and nano-photonics. Here we discuss the use of OMVPE on nonplanar, structured substrates for the fabrication of semiconductor quantum nanostructures for nano-photonics studies and applications.

The quantum nanostructures we investigate are grown on patterned, nonplanar (100) or (111)B GaAs substrates, structured using optical or electron beam lithography. The nature of the MOVPE process and the resulting characteristic of the grown heterostructures depend closely on the dynamics of the metallicorganic precursor migration and decomposition, as well as on adatom diffusion and incorporation into the growing crystal. These, in turn, are significantly modified by the surface non-planarity of the patterned substrates. In particular, highly concave or convex topography features introduce controlled variations in the surface chemical potential. This gives rise to capillarity-induced surface fluxes of adatoms that tailor the local growth rate on a nanometer scale. An example is shown in the Figure, which depicts Monte-Carlo simulations of GaAs growth on a (111)B GaAs substrate patterned by an inverted, tetrahedral nano-pyramid (several 100nm-diameter) \cite{1}. Capillarity leads to thickening of nm-thick grown layers at the concave parts of the substrate. Thus, an otherwise thin, 2D quantum well (QW) GaAs/AlGaAs or InGaAs/GaAs heterostructure can be transformed into a 1D quantum wire (QWR) or 0D quantum dot (QD) formed along the wedges or bottom corner of the inverted pyramid. Several examples of the formation of such low-dimensional quantum nanostructures with this approach will be presented.

The 2D and 3D quantum confinement of charge carriers, induced by the QWR and QD heterostructures, can be used to tailor their electronic and optical properties, such as the carrier mobility or optical absorption and emission spectra. Moreover, incorporating such QWRs and QDs inside photonic nano-cavities and nano-waveguides can further modify light-matter interaction in these systems and generate new classes of photonic devices and circuits. One important example is the integration of QDs with nano-photonic cavities, e.g., those based on membrane photonic crystal (PhC) cavities. For such studies, it is essential to match the position, emission spectrum and optical polarization of the QD to those of the particular cavity mode to which it would be coupled. The pyramidal QDs discussed here are especially suited for such integration because of the virtually perfect (~1nm) controllable position they offer, reproducible emission spectra and high structural in-plane symmetry. Examples of the integration and the resulting optical properties of pyramidal QDs integrated with PhC cavities and waveguides will be discussed \cite{2}. Since semiconductor QDs can emit single photons “on demand”, such integrated photonics schemes might yield novel photonic circuits for performing on-chip manipulation of single photons and other non-classical states of light.

References:
Section 1

Theoretical Bases of Chemical Engineering
Only fifty years ago in the entire world Ethanol was produced from petrochemical feedstock. For this case were created many pyrolysis factories. These factories are used for thermal cracking petrol crude for generation a number of petrochemical products including an Ethylene. Till the recent time Ethylene was used for generation of Ethanol. However, everything had changed when Ethanol was started to generate using natural crude. High capacities of Ethanol production decreased Ethanol prices. In the same time Ethylene prices continuously increased because of indispensability of Ethylene for generation necessary petrochemical products such as: Polyethylene, Ethylbenzene, Ethylene oxide, Vinyl acetate, Vinyl chloride. Finally in the present time here is almost no one factory, that use Ethylene for Ethanol production (One factory in a whole Russia). That is why raised a question about reverse process: dehydration Ethanol to Ethylene.

In the present time, many scientific institutes have already cared a lot off laboratory experiments for getting Ethylene from Ethanol, high quality catalysts were created, industry production Ethylene from Ethanol was organized by company Braskem in Brazil. Now the process of generation Ethylene via Ethanol was taken into account in Russia and Ukraine as well. As was shown by analysis results, products of reaction dehydration Ethanol to Ethylene have a quite specific composition: hydrocarbon fractions C1 – C4, Oxygenates, Carbon oxides and Hydrogen. That’s why it’s very important to create a high selectivity catalysts to decrease waste reaction products. High selectivity catalysts allow to minimize operation units of products separation system equipment.

Nevertheless, such types of feedstock for Ethylene recovery still wasn’t taken into account in Russia. Moreover, target is to achieve Ethylene purity specification 99.9 % w. Also here is another long discussed question – it’s to design low capacity technology of Ethylene production (15000-30000 tons/year) that very useful, for example, for copolymers production. That’s why the most important demands for technology are high purity of Ethylene and simplicity and cheapness of designed technology.

In this case, design of technologies of Ethylene recovery from products of dehydration Ethanol to Ethylene has been started. Finally, a number of technologies were designed. Each of technologies has its own specific factors and allow to achieve high Ethylene purity specification. Each of technologies for Ethylene recovery from Ethanol dehydration reaction products include a number of new technical solutions for processes of Ethylene recovery, such as:

– Ethylene recovery without using low temperature separation system (below 25 °C);
– the opposite way – using ammonia refrigeration system for Ethylene recovery;

Each of technologies can be competitive and may be realized in an industry.
CHANGING THE RHEOLOGICAL PROPERTIES OF THE VISCOUS HCl
BY REACTING WITH THE DOLOMITE

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The acidic treatment of oil- and gas-saturated reservoir with carbonate (CaCO3, 
CaMg(CO3)2) matrix is the main method of hydrocarbons inflow intensification. The high rate of 
concentrated HCl reaction with calcite (CaCO3) and dolomite (CaMg(CO3)2) results in large 
caverns generation in the bottomhole formation zone. A new trend in the acid treatment of 
carbonate reservoir is gelling of HCl (12 wt %) by surfactants, such as carboxybetaine. The 
changing of rheological properties of gelled HCl (12 wt %) solutions with CaMg(CO3)2 at high 
mineralization of water \( (C_{NaCl} = 150 \text{ g/l}) \) has not found. Gelling of HCl (12 wt %) was carried 
out by surfactant – carboxybetaine (6.5 wt %) at NaCl = 150 g/l. Viscosity of the solutions was 
controlled on the rotary viscosimeter HTHP-5550 (Ametek Chandler Engineering, USA). 
Experiments to establish the viscosity of a gelled acid were performed at shear rates according to 
API RP 39 standards (25-50-75-100 \text{s}^{-1}). Changes of micelles of surfactant were get on the laser 
diffraotmeter Microtrac Zetatrac, cuvette 10 cm\(^3\), for 6 minutes. X-ray powder diffraction 
analysis of dolomite samples was performed on a DRON-7 diffractometer using Ni-filtered 
Cu\(K\alpha\) radiation. X-ray diffraction patterns were processed using the PDWin program package 
with reference to the PCPDFWin database.

Aqueous 12 wt % hydrochloric acid has dynamic viscosity of 1.230 mPa·s. Stable acid 
gels are formed when carboxybetaine (6.5 wt %) is added to the aqueous acid. These gel 
gardless of their compositions, shows non-Neutonian flow as intrinsic to high-pseudo-plastic 
liquids. The gel containing 12 wt % HCl, 15 wt % NaCl, and 6.5 wt % carboxybetain has 
viscosity 99.8-64.2-57.6-50.1 mPa\(\cdot\)s, when share rates are 25-50-75-100 \text{s}^{-1}.

Fig. 1. Micelle sizes of acid gel after (a) and before (b) reaction with carbonate.

Reaction of acidic gel with dolomite leads to change of rheological properties of liquid. 
The dynamic viscosity of the gel increases significantly. The complex micellar system exists in 
solution before acid-carbonate interaction. More than 60% micelles of solution have a size in the 
range of 1-10 nm (Fig. 1a). These micelles have spherical shape. Aggregates with sizes 200-1200 
nm are worm-like micelles whose presence provides enhanced viscosity of solution. Micelle 
particles have a size more 2000-5000 nm after neutralization of HCl by dolomite (Fig. 1b). All 
spherical micelles of surfactant transform into worm-like micelles when the cations Ca\(^{2+}\) are 
arose in the composition. Change of micelle structure correlates with the increase of solution 
viscosity. Dynamic viscosity of neutralized solution 12 wt % HCl, 15 wt % NaCl, and 6.5 wt % 
carboxybetain is 627.4-511.3-398.7-204.6 mPa\(\cdot\)s, when share rates are 25-50-75-100 \text{s}^{-1}.
THE NEW THERMODYNAMIC METHOD OF CONSTRUCTING GENERALIZED DEPENDENCIES IN THE DIMENSIONLESS FORM

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A new thermodynamic method of constructing generalized dependency properties of various hydrocarbons, based on the principle of minimal characteristic functions. As you know, most of generalization techniques are finding dependencies between the desired properties of substances on the arguments in the dimensionless form. As in the construction of the scale ratio of the dimensionless parameters selected values of different states depending on the substances constructing ideas: the parameters of the critical point, the properties of substances with excess pressure parameters, the parameters of the triple point, the characteristic dimension. It is assumed that these states are thermodynamically stable. However, steady state thermodynamics determines the state in which characteristic features are minimum. The search for such a state were carried out in the phase transition liquid-vapor. This is explained by the fact that the definition of the process parameters and conditions on the saturation lines is limited by specifying either P or T. In connection with the selection of the scale of the search area is not hard to find the characteristic function. That need to be explored. This free energy, which in absolute value is numerically equal to the expansion phase of the transition process. The study of this function it possible to find the temperature (denoted by its Tm) at which $\Delta f$ (free energy change) has a minimum value. It turned out that the Tm is related to the critical temperature $T_k$ simple relation:

$$ T_m = 0.76 \times T_k $$  \hspace{1cm} (1)

For all hydrocarbons with a range of 2%. Those. This temperature corresponds to a stable state, and therefore, at this Tm to choose the scale of relations in the construction of generalized dependencies, which can be represented as:

- for the parameters characterizing the phase transition ($\Delta H, \Delta S, \Delta U, \varepsilon$):

$$ \frac{\Delta \chi}{\Delta \chi m} = f \left( \frac{\Delta \rho}{\Delta \rho m} \right) $$  \hspace{1cm} (2)

- for value. Characterized by state agents on the saturation lines:

$$ \frac{\chi}{\chi m} = f \left( \frac{p}{\rho m} \right) \text{ or } f \left( \frac{T}{T_m} \right) $$  \hspace{1cm} (3)

Confirmation of the correct starting positions in the search results are the scale ratio of the dimensionless relationships for various properties other than the simplest form of presentation and the good agreement between the experimental results of different authors.
Mixing of particulate solids is used in a wide range of industries. Very often the homogeneity of obtained mixtures is a key property that defines the quality of target or half-finished products. However, in mixing of dissimilar particulate solids, it is practically impossible to reach the homogeneous mixture because of the phenomenon of dissimilar particles segregation. The limit homogeneity exists, which depends on the ratio of different particles properties and conditions of mixing. A cell model using the theory of Markov chains was developed to describe the kinetics of mixing of dissimilar components. It is based on the recurrent matrix equalities

\[ S_{j}^{k+1} = P_{j}S_{j}^{k} \]

where \( j \) is the number of component, \( S_{j} \) is its state vector that describes the \( j \)-th component distribution over the cells representing a mixture operating volume, \( P_{j} \) is the matrix of transition probabilities that depends not only on the \( j \)-th state vector but also on the state vectors of all surrounding components (a non-linear model), and \( k \) is the current number of time transition of small duration. The model allows describing the mixing kinetics of each component and the entire mixture. Numerical experiments show that the optimum mixing time exists that gives the minimum value to the non-homogeneity. However, this optimum time is different for each component and the entire mixture. At the same time, these optimum times and minimum non-homogeneities strongly depend on the initial state of the components, i.e., on the way of their loading into a mixer. A common way of loading components is loading them one above another at one approach. However, it is the worst way to fight the negative influence of segregation. The maximum mixing quality can be strongly improved and the optimum mixing time can be strongly reduces if to load the components as sandwiches, each of which contains the components in the same proportion as the entire mixture. The influence of the sandwiches number on the maximum mixture quality and optimum mixing time was found using the model based on Eq.(1). A new design of vibration mixer that allowed multi-sandwich loading was proposed and tested experimentally.

However, while the mixing time decreases with growing number of sandwiches the loading time increases. In order to estimate the total productivity of a mixer at given mixture quality the following objective function can be used:

\[ K = K_{\text{mix}}(m) + K_{\text{load}}(m) = K_{\text{mix}}(m) + bm \]

where \( K \) is the duration of the total cycle of mixing, \( K_{\text{mix}} \) is the duration of mixing proper, depending on the number of sandwiches \( m \), \( K_{\text{load}} \) is the duration of loading that is taken directly proportional to the number of sandwiches with the proportional coefficient \( b \). It is shown that, at given mixture quality, the optimum number of sandwiched exists that gives the minimum value of \( K \), i.e., of the mixer productivity.

Thus, the proposed approach allows improving the quality of mixture of dissimilar particulate solids and reducing the mixing time, and the proposed Markov chain model allows estimating rational regime and design parameters of a mixer.

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The paper presents a new generalized method of calculation for dynamic viscosity, based on fundamental thermodynamic principle of minimal characteristic functions. In the study of the features of the phase transition liquid-vapor it has been found that in the phase of transition there is some temperature $T_m$ at which the free energy has a minimum value. At this temperature, the examined object, of course, is stable state.

Using the properties of matter at $T = T_m$ (in our case, viscosity) allowed the desired property in the reduced form to submit:

$$\frac{\Delta \eta}{\Delta \eta_m} = f\left(\frac{1 - \frac{T}{T_m}}{1 - \frac{T_m}{T_m}}\right)$$  \hspace{1cm} (1)

This difference in properties is at saturation lines.

For properties on the border lines of the generalized dimensionless form of presentation is as follows:

$$\left(\frac{\eta'}{\eta'_m}\right) = f\left(\frac{T}{T_m}\right)$$  \hspace{1cm} (2)

$$\left(\frac{\eta''}{\eta''_m}\right) = f\left(\frac{T}{T_m}\right)$$  \hspace{1cm} (3)

The experimental data in the form of (1)-(3) has shown that for better convergence results you have to enter a parameter correlating these factors acentricity Pitzer.

In processing the experimental data on the equations (1)-(3) in view of correlating parameter yielded approximate formula to calculate the error of calculation which does not exceed 3%, 7% and 5% respectively.

Further links were established between the scales: $\eta'_m, \eta''_m, \Delta \eta$ on the molecular weight of the compound, it possible to determine the temperature dependence of these properties on the chemical structure of the compound.
THE STUDY OF DIMETHYLCYCLOSILOXANES FORMATION REGULARITIES IN HETEROYPE HYDROLYSIS OF A DIMETHYLDIALKOXYSILANE

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It is well known that the question of the relationship between linear and cyclic products in the hydrolytic polycondensation (HPC) organochlorosilanes and organoalkoxysilanes was discussed repeatedly during the formation at the beginning of the production of silicones and discussed today. In the late 90-ies, the results published in the area of macrokinetics of heterophase hydrolysis of a diorganodichlorosilanes allowed to purposefully steer the process toward the formation of only the cyclic or linear products [1]. Due to the fact that the difference in reactivity of organoalkoxysilanes and organochlorosilanes may cause a completely different ratio homofunctional (HMPC) and heterofunctional condensation (HTFC), affecting the composition of hydrolysis products was of interest to study the HPC diorganodialkoxysilanes.

The report provides comparative data on the formation of linear and cyclic products in HMPC (CH₃)₂Si(OH)₂ and partial hydrolysis (PH) (CH₃)₂Si(OR)₂ (R = Me, Et, iPr, Bu). This problem was solved by studying the composition of hydrolysis products (CH₃)₂Si(OR)₂ depending on the ratio water/monomer at different temperature, concentration of catalyst, nature of solvent (such as dioxane, acetone, acetonitrile, n-hexane, nitromethane, THF, MTBE, toluene, ethyl acetate), order and rate of input of reactants. The GLC method was used to estimate composition of products and nature of chain.

As a result, we have found that the quantitative yield (close to 100 %) of dimethylcyclosiloxanes is achieved under non-equilibrium conditions on the mechanism HTFC when the molar ratio of the reactants [H₂O]/[(CH₃)₂Si(OR)₂] = 1, the final composition of the products of hydrolysis depends little on temperature, concentration of catalyst, nature of solvent (such as water-miscible and not miscible), the nature of the functional group, the order and speed of input of reactants. The resulting investigation of the laws of the hydrolysis of (CH₃)₂Si(OR)₂ can be the basis for an effective technology of obtaining of organomethylcyclosiloxanes.

Fig. 1. The dependence of the composition of the products (S, mole fraction) on conversion of functional groups in the hydrolysis of (CH₃)₂Si(OR)₂ in various solvents (n – the degree of polymerization oligomers, Lₙ – linear oligomers, Dₙ – cyclic oligomers).

Reference:
OPTIMIZATION OF THE SYNTHESIS OF METHYLSILSESQUIOXANE
BY THE SIMPLEX-PLANNING METHOD

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Polymethylsilsesquioxanes (PMSSQ) unlike other organosilsesquioxanes have several advantages:
1. The rapidity of curing at low temperatures;
2. Thermosetting in the absence of catalysts. This leads to an improvement in the thermal stability of both the resin and based materials;
3. The good arc resistance and excellent dielectric properties.

Earlier, the simplex method of planning was used in order to minimize reagent consumption in the hydrolysis of methyltrichlorosilane for the synthesis of PMSSQ[1]. In this paper the initial concentration of the reactants were chosen by the method of random balance. To achieve optimum was performed more than a hundred steps of the simplex. In our work to optimize the synthesis PMSSQ of methyltriethoxysilane (MTEOS), we applied the method of simplex-planning, which takes into account the heterophase nature of the process of hydrolysis of MTEOS. The phase state of the system consisting of water, solvent and products of hydrolysis of MTEOS have been determined experimentally and calculated by the NRTL equation [2]. As simplex factors were chosen gross composition of the reaction system, the initial values which provide the required molecular weight and structure of the organosilsesquioxanes. Optimal values of the factors were achieved for 9 steps, thanks to the correct choice of the beginning of movement.

As a result, the optimal conditions for obtaining PMSSQ (analogue of resin KO-812) designed with a yield of more than 90%, achieved the required gelation time (~ 10-15 minutes) and the desired concentration of resin in the solution (30-40%). The shelf life of the resulting resin solution is not less than 3 months.

References:
INVESTIGATION OF ACTIVITY OF NANOPOWDER CALCIUM OXIDE AS BASE CATALYSTS FOR THE SYNTHESIS OF SOYBEAN OIL METHYL ESTERS

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2 Lobachevsky State University of Nizhny Novgorod, National Research University, Nizhny Novgorod, Russia

Finding alternatives to fossil fuels has attracted a worldwide interest in recent years due to limited reserves of traditional fossil fuels, the instabilities of the crude oil price and the concerns over greenhouse gas emissions. Biodiesel, a mixture of fatty acid methyl esters (FAME) is a promising substitute to diesel fuels due to its environmental benefits and the fact that it might be synthesized from renewable resources. It is usually produced by methanolysis of triglycerides in the presence of a catalyst. Calcium oxide (CaO) is one of the most common used heterogeneous base catalysts for the transesterification of vegetable oil.

In this paper the catalytic activity of nanopowder CaO was investigated. Moreover, comparison of nanopowder CaO, powder CaO and calcium diglyceroxide was carried out in the transesterification reaction of soybean oil with methanol.

Nanopowder CaO showed higher activity than powder CaO in the reaction of transesterification of soybean oil with methanol. Using powder CaO as a catalyst in the transesterification reaction, yield of FAME did not exceed 12% after 60 min; while using nanopowder CaO as a catalyst of the process, yield of FAME was 50% after 60 min and 98% after 120 min. This increase in catalytic activity of nanopowder CaO is connected with the fact that the surface area of nanopowder CaO is significantly more than the surface area of powder CaO (table).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nanopowder CaO</th>
<th>Powder CaO</th>
<th>Calcium diglyceroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total surface area (m²/g)</td>
<td>32.35</td>
<td>4.31</td>
<td>1.2</td>
</tr>
<tr>
<td>Crystal size (nm)</td>
<td>17.30</td>
<td>142.00</td>
<td>136.00</td>
</tr>
<tr>
<td>Basic strength (H_)</td>
<td>6.8 &lt; H_ &lt; 17.2</td>
<td>6.8 &lt; H_ &lt; 9.3</td>
<td>6.8 &lt; H_ &lt; 18.4</td>
</tr>
</tbody>
</table>

Calcium diglyceroxide has a smaller surface area than the nanopowder CaO one. However, using calcium diglyceroxide, the yield of methyl esters was 57% for 60 min. The high yield of methyl esters is explained by the fact that the calcium diglyceroxide is the general active phase in FAMES production when calcium oxide is used as a catalyst [1].

The fact that basic centers of nanopowder CaO react with glycerin to form calcium diglyceroxide was found out during the reaction of transesterification. Using nanopowder CaO can reduce the formation time of calcium diglyceroxide, because of the presence of more available basic centers. Thus, calcium diglyceroxide is the main catalyst of transesterification of triglycerides despite the form of CaO (powder CaO or nanopowder CaO). Using of nanopowder CaO can only reduce the induction period of reaction.

Reference:

Extractive distillation (ED) is the common method for the separation of ternary azeotropic mixtures. In this study different schemes extractive distillation involving three columns have been considered. The conventional separation sequence (I) consist of three distillation columns: 1 - extractive distillation (concentration in the distillate the most volatile component), 2 - separating second component, 3 - regeneration of heavy entrainer. Scheme II involves columns: 1- extractive distillation, 2 - isolation of selective agent, 3 - separation of zeotropic binary mixture.

Pre-concentration usually used when the need to separate by ED binary azeotropic mixtures containing water. The preliminary dehydration feasibility of ternary azeotropic mixtures methanol (M) - tetrahydrofurane (THF) - water and methanol (M) - acetonitrile (A) - water (W) are discussed. The separation of these mixtures (3.2.0-2b in Serafimov's classification) has a practical significance [1]. Glycerol can be used as extractive agent for mixtures containing water [1]. In addition to the standard scheme I, considered another option II: 2 - separation of the glycerol, 3 - distillation of methanol - water mixture.

In the software package Aspen One 8.0 calculation ED-flowsheets were carried out for mixtures M - THF - W and M - A- W at 101.32 kPa. Modeling of phase equilibria performed using NRTL-RK (Non Random Two Liquid model, Redlich-Kwong Equation of State). The original ternary mixtures contain various amounts of water: (0.392; 0.408; 0.2) and (0.049; 0.051; 0.9) for M-THF-W; (0.723; 0.177; 0.1) and (0.161; 0.039; 0.8) for M-A-W.

Total energy consumptions (∑ - summary reboiler’s heat duty of all distillation columns) for schemes I, II (without pre-concentration column) are given in Table for separation of 100 kmol/h ternary mixtures. Total energy consumptions are 1.95 - 2.9 times less for mixtures with high water content for both schemes and both ternary mixtures. Therefore, schemes with preliminary concentration a priori to be more energy-intensive.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>M - THF - W</th>
<th>M - A - W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme</td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>x_W, m.fr.</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>F_Gl, kmol/h</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>∑, kW</td>
<td>4778.0</td>
<td>2266.7</td>
</tr>
</tbody>
</table>

Ternary mixtures enriched water, characterized by large relative volatility THF (or A): so you need to enter fewer glycerol. It makes sense use mixture water - glycerol for ED both mixtures with low water content.

Acknowledgements
The study was conducted with financial support of RFBR, research project No. 14-03-00523.

Reference:
DESCRIPTION OF KINETIC MODEL OF FERMENTATION CATALYSIS

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The scheme of fermented catalysis are include reversible of composition of intermediate complex of ferment (E – of aminalonovaya acid) with reactive material (substratum S – of amino acid) and conversion thereof of complex in products of reaction (P – of glitsin, al’dinin and dr.):

\[ E + S \xrightarrow{k_1} E S \xrightarrow{k_2} E + P, \quad (1) \]

where \( E S \) - intermediate complex, \( k_1 \) – constant binarymolecular binarychemical reaction, \( k_{-1} \) – constant reverse reaction, \( k_2 \) – constant irreversible onemolecular reaction. The approach of pseudobalanse of approach at this scheme (at condition \( k_2 \ll k_{-1} \)) with accounting of material of balance:

\[ [E] = [E]_0 - [E S], \quad (2) \]

where \([E]\) – concentration of ferment, \([E]_0\) - initial of concentration, \([E S]\) – concentration of intermediate complex. The equation (1 – 2) permit velocity of composition of product over initial concentration of ferment and current concentrations of substratum are putted:

\[ r = \frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_S + [S]}, \quad (3) \]

where \([P]\) – concentration of product, \([S]\) - concentration of substratum, \(K_S = k_1 / k_{-1} = [E] [S] / [E S] \) - substratum constant. At increase of concentration of substratum velocity of reaction (3) at marginal account – \( r_{\text{max}} = k_2 [E]_0 \) are aimed. The velocity of thereof reactions with maximum velocity of correlation are bonded:

\[ r = \frac{r_{\text{max}} [S]}{K_S + [S]}, \quad (4) \]

Usual in experiment relation of initial velocity of ferment reaction (4) from initial concentration of substratum \( r_0 = f([S]_0) \) are measure.

Offer kinetic model for maximum of outcome of product (glitsin, al’dinin and dr.) and may for designing of reactoral equipment of given process are employed [1 - 3].

The scheme of fermented catalysis for conversion of ferment (aminalonovaya acid) and substratum (amino acid) in products of reaction (glitsin, al’dinin and dr.) most efficient in liquidphase reactors are driven.

References:
NANOSTRUCTURED TITANIUM SILICALITE IS AN EFFECTIVE CATALYST FOR THE EPOXIDATION OF α-OLEFINS WITH HYDROGEN PEROXIDE

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²LLC “Scientific Research & Development Center Sintez” (R&D Center “Sintez”), Moscow, Russia
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Among the α-epoxides propylene oxide, epichlorohydrin (ECG) and glycidol (1,2-epoxypropanol) are the most common products or monomers for industrial organic synthesis. Due to the peculiarities of the α-epoxides structure they could react with different classes of compounds, which allow to obtain products that are in demand in many industries (epoxy resins, lacquers, adhesives, rubber, etc.). However, the used methods have significant disadvantages: low target products yield, the formation of significant quantities of troublesome side products, sewage pollution, etc.

A promising method for producing propylene oxide, ECG and glycidol is liquid-phase catalytic epoxidation of propene, allyl chloride and allyl alcohol with an environmentally friendly oxidant - hydrogen peroxide.

We have developed a catalyst – nanostructured titanium silicalite –, the optimum conditions, the kinetics of liquid-phase epoxidation of allyl chloride and allyl alcohol with hydrogen peroxide in methanol, the kinetic model of the processes [1, 2].

To determine kinetic parameters and to verify the adequacy of the models conducted a series of experiments, varying the initial conditions. It was varied the height of the catalyst layer, flow rate, temperature (30-60°C), initial concentration of hydrogen peroxide, propene, allyl chloride and allyl alcohol and methanol. Statistical analysis showed that at a significance level of 0.05, the proposed kinetic model adequately describes the experimental data and enables to predict the composition of the reaction mixture in a wide range of variables at different conversions of hydrogen peroxide.

Acknowledgements

This study was supported by the Ministry of Education and Science of the Russian Federation (grant agreement No. 14.577.21.0093, unique project identifier RFMEFI57714X0093).

References:

FEACHERS OF CALCULATION OF MATERIAL BALANCE OF QUATERNARY SPLITTING SYSTEM SEPARATION FLOWSHEET

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The research of phase diagram of multicomponent multiphase systems and flowsheets of their separation is a multidimensional task. The presence of azeotropes and separatric manifolds leads to the formation of recycles in flowsheet and complication of balance task. Method proposed in [1] is directed to the solution of this problem. The main idea of the method is determination of the number of freedom degrees (F) that depends on number of variables (amount and composition of all material streams of flowsheet) and number of independent equations (equations of material balance of apparatus and flowsheet, conditions of vapor-liquid and liquid-liquid equilibrium, requirements to the purity of products). Previously [1-2] it was shown that the number of freedom degrees of the linear part of the flowsheet (without recycle) is zero. So we can formulate the following rule for the flowsheet of separation of multicomponent mixtures: the number of freedom degrees of a flowsheet is equal to the sum of the numbers of degrees of freedom of the separation complexes included in flowsheet. Thus to determine F and solute balance task it is necessary to make decomposition of flowsheet, i.e. to break it into separate fragments: the various functional complexes (the number of free variables of which are already known) and linear part.

Model system 1-2-3-4 containing two pairs of component with limited mutual solubility (1-2 and 3-4) was considered as an example. Phase diagram of the system and flowsheet of its separation is presented in Figure. Flowsheet can be divided into three parts: I and III – heteroazeotropic distillation complexes (with recycles); II – single column (linear part of flowsheet). Authors [1] have shown that number of freedom degrees of such complexes (I and III) including two distillation columns and florentine vessel is equal to zero as well as for linear part of flowsheet (I). So number of freedom degrees of the whole flowsheet will be also zero.

Phases diagram (a) and flowsheet of separation (b) of quaternary system.

Method was illustrated on the example of a number of model and real four- and five component systems that proved its validity.

Acknowledgements: The research was made under the financial support of Russian Science Foundation (project № 16-19-10632).

References:
The aim of this work was to study the influence of the value and composition of the recycle stream on the amount of energy consumption, required for the achievement specified values of conversion and selectivity in the reactor-separation unit system, on the example of next consecutive reversible reaction

\[ A \leftrightarrow B \leftrightarrow C, \]

wherein component B is the desired product.

At the first stage, the calculation of a chemical reactor, which was an element of the recirculation circuit, was performed by varying the value of the total recycle flow rate and its composition. It was considered that the separation unit is able to form the recirculation and output streams of any given composition. As a result of calculations it was discovered, that the whole set of stationary states are implemented in the system, corresponding to the same specified values of conversion and selectivity, but at different values of the rate and composition of recycle stream. Obviously, each such stationary state will meet its energy costs, the value of which is determined by the type of separation process. By using rectification in separation unit, main energy costs are determined by the amount of heat applied to the reboiler of a column. In this case, increasing of the recycle stream will increase the load on the column, which in turn will lead to a growth of energy consumption (the amount of heat supplied to the reboiler). On the other hand, for high values of recycle streams that provide specified values of conversion and selectivity, requirements for the quality of separation are reduced, that can decrease energy costs by reducing the reflux stream. Thus there is the optimization problem in which the objective function is energy costs \( Q \), and the optimization parameters are the values of the total recycle stream and a reflux stream. When carrying out optimization of the recirculation system reactor-distillation column an ideal model reactive mixture A, B and C was considered with the following boiling points assignment: \( t_A^0 = 9.42 \, ^\circ C, \ t_B^0 = 35.93 \, ^\circ C, \ t_C^0 = 27.83 \, ^\circ C \). Calculations were performed with the following initial data: input value \( f_A = 100 \, \text{kmol/h} \), the rate constants \( k_1^+ = k_1^- = k_2^+ = k_2^- = 100 \, \text{kmol/(m}^3 \text{h)} \), reactor volume \( V = 3 \, \text{m}^3 \), number of theoretical stages - 34, the feed tray - 17th from the top.

As a result of the series of calibration calculations we found the optimum process conditions (values of the recycle stream and the reflux ratio) to provide the desired amount of conversion 99% and selectivity of 95% at minimal energy costs.
The isotherms of adsorption of DST-30 were obtained into small and large fractions of chalk on the mixture fraction in a ratio of 1:1, and on the mixture ratio corresponding to the maximum combinatorial entropy of mixing (in this case, 87.4 wt.% the coarse fraction). Isotherms show that the highest values correspond to the adsorption of most small fraction of the adsorbent, which is associated with a large unsaturated adsorption field of small particles. Adsorption on mixtures taken in an “optimal” ratio in the region of concentrations up to 0.8%, exceed the values of adsorption of the small fraction.

In the mixture, in which the ratio of components is sub-optimal (1:1), the values of adsorption are close to those for the coarse fraction of the adsorbent.

The free energy determines not only the physical and chemical properties of the system in bulk and on the surface, but also its stability, characterized by, for example, strength. Table 1 shows the strength values of unfilled and filled DST-30, depending on the elongation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DST-30 + 10% of the coarse fraction of chalk</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε, % P&lt;sup&gt;exp&lt;/sup&gt;, MPa</td>
<td>200 0,22</td>
</tr>
<tr>
<td>Sample</td>
<td>DST-30 + 10% of the small fraction of chalk</td>
</tr>
<tr>
<td>P&lt;sup&gt;exp&lt;/sup&gt;, MPa</td>
<td>0,61 0,83 0,93 1,1 1,32 1,88 3,02</td>
</tr>
<tr>
<td>Sample</td>
<td>DST-30 + 10% of a mixture of chalk fraction (50% by weight of the coarse fraction)</td>
</tr>
<tr>
<td>P&lt;sup&gt;exp&lt;/sup&gt;, MPa</td>
<td>0,90 1,12 1,28 1,60 2,31 3,27</td>
</tr>
<tr>
<td>Sample</td>
<td>DST-30 + 10% of a mixture of chalk fraction (87,4% by weight of the coarse fraction)</td>
</tr>
<tr>
<td>P&lt;sup&gt;exp&lt;/sup&gt;, MPa</td>
<td>1,9 2,1 2,3 2,6 2,9 3,5 4,6</td>
</tr>
</tbody>
</table>

As expected, the introduction of the block-copolymer filler reduces the strength of the system.

For the system of barium sulfate - Silicone rubber is calculated the optimal ratio of the two filler components in a wide range of volume ratio V1/V2 with different filler content by volume in a polymer matrix. Table 2 shows the dependence of the optimum molar fraction of the component from the volume ratio of the filler particles.

<table>
<thead>
<tr>
<th>V&lt;sub&gt;1&lt;/sub&gt;/V&lt;sub&gt;2&lt;/sub&gt;</th>
<th>1</th>
<th>0,5</th>
<th>0,25</th>
<th>0,1</th>
<th>0,05</th>
<th>0,025</th>
<th>0,01</th>
<th>0,005</th>
<th>0,0025</th>
<th>0,001</th>
<th>0,0005</th>
<th>0,00025</th>
</tr>
</thead>
<tbody>
<tr>
<td>x&lt;sub&gt;1&lt;/sub&gt;</td>
<td>0,5</td>
<td>0,44</td>
<td>0,35</td>
<td>0,25</td>
<td>0,206</td>
<td>0,17</td>
<td>0,135</td>
<td>0,115</td>
<td>0,099</td>
<td>0,082</td>
<td>0,072</td>
<td>0,064</td>
</tr>
</tbody>
</table>
Xylenols find a broad application in synthesis of the materials possessing a complex of valuable properties (paints-and-varnishes, thermoplastics, non-inflammable oils, medicines, low-toxic pesticides, "clever" materials, plasticizers, surfactants). However, effective methods of synthesis of xylenols are absent now. The most extensive use was gained by the practice of industrial receiving of xylenols from fractions of the coal tar received at coke-chemical production and from oil refining waste where the amount of xylenols is small (the hundredth and even thousandth shares of percent). Rather new synthetic methods of receiving xylenols, such as sulfuration, alkylation of cresols, dinitriding of xylidines, are multi-stage and are characterized by low exits of target products, high cost of their receiving and a big consumption of auxiliary materials. All of this results in a substantial limit of their industrial realization and, thus, constrains the development of production of the materials which possess a complex of valuable properties and are needed in the modern industry and the national economy. Search and development of selective and economic methods of receiving xylenols which are based on the use of petrochemical raw materials is a relevant objective.

In the furtherance of this goal, the innovative three-phasic method of receiving 3,4-xylenol has been offered by G.N. Koshel and others [1]. It includes the following stages: alkylation of ortho-xylene and receiving a 4-isopropyl-ortho-xylene (4-IPOX), its oxidation, decomposition of hydroperoxide 4-IPOX with incidental receiving acetone. The stages of oxidation 4-IPOX and decomposition of its hydroperoxide have been currently worked out. However, the initial, key stage – alkylation of ortho-xylene – is underexplored. For its industrial realization it is necessary to study the possibility of extremely selective receiving of 4-IPOX in the conditions of thermodynamic and kinetic control.

Research of processes of alkylation of an ortho-xylene by propylene in the presence of a macroporous sulfocationite and transalkylation of the received reaction mass in the presence of AlCl₃ has been conducted. Reaction mixture was moved to an equilibrium state in the wide range of temperatures, contents of reagents and amount of a catalyst. As a result, its equilibrium compound has been studied in a series of experiments.

As a result:
1) for the stage of alkylation: dependence of the composition of reaction mass on a reagents ratio is defined;
2) for the transalkylation stage (in the range of 291-353 K under concentration of AlCl₃ 1,35 up to 2,34 % mass): the kinetics of the proceeding transformations is studied up to the equilibration of the entire system. Thermodynamic characteristics of the isomerization 3-IPOX in 4-IPOX and realkylation of a 3,5-diisopropyl-ortho-xylene on an ortho-xylene with formation 4-IPOX are defined.

The obtained experimental data are the basis for the comparative analysis of various technologies for selective receiving a target 4-IPOX.

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

Reference:
The polyesters recycling is one of the most actual ecological problems in our world. In Russian Federation, the most widely distributed polyester is polyethylene terephthalate (PET). In 2014 PET production in Russia was 432,000,000 tons per year.

PET decays about 120-150 years and at that moment there is no an efficient method, that will allow to recycle this type of plastic with benefit. Usually it is being burned, or transformed with using extruder into materials, which have rather less valuable mechanical characteristics.

PET is used as material for a packaging tape, a plastic tare and material for clothes. Inventing of a new way of recycling will solve a problem with used clothes conversion. Furthermore, such effective method will deal with one more important ecological problem – the problem of “bottle islands” (e.g. Great Pacific garbage patch).

We offer a non-catalytic method of recycling. It is in a hydrolysis of polyethylene terephthalate. As a product, we obtain the monomers of polyethylene terephthalate – terephthalic acid and ethylene glycol. The hydrolysis of polyethylene terephthalate is conducted under subcritical conditions.

Environmental Benefits from the closed-loop recycling of PET plastic (data source: US EPA, 2006): energy savings 53 MBTUs/ton, avoided GHG emissions 0.42 (MTCE/ton of recovered material).

Critical condition is the special condition of compound when a liquid and its vapor can coexist. Under these conditions, abruptly change parameters, such as heat capacity, viscosity, the dielectric constant, etc. Compounds under these conditions (also known as supercritical fluids) have special chemical properties. E.g. using supercritical water to destruct industrial waste, supercritical fluid as an extractant, as a solvent, using in coal refining, organic synthesis, soil and wastewater purification, supercritical chromatography etc. Moreover, the course of reaction flow is also changes in these conditions. That is why we chose this method of experiments conducting.

In this research has been considered one of the possible way of chemical recycling of PET-bottles. The influence of temperature, contact time and reagent ratio to the conversion degree of polymer and process selectivity was examined. There was an experiment, that showed us a correlation between density of system and reaction output. Also, have been carried an experiment with inert agents, which had increased density of system. By special experiments were visualized processes occurring in the system at all stages of decomposition colorless and colorized PET-bottles. Chemical process of recycling allows to remove pollutants (e.g. dyestuff and bleach). It allowed us to find the relatively simple technical solutions for separating monomers from dyes. On the basis of this research is planned way in the development of technology, which, according to our estimates, will be able to compete with modern solutions in this area.

Acknowledgements

This work was financially supported by the Ministry of Education and Science of Russian Federation within the framework of the basic part of state task of Samara State Technical University (project code 1708).
IDENTIFICATION OF CLAUS REACTION PRODUCTS OVER THE CATALYST

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The Claus process is the final stage of processing of oil and gas if the hydrogen sulfide is present therein. The catalytic stage of the Claus process consists of passing a mixture of H₂S and SO₂ in a 2:1 mole ratio over the catalyst bed (Al₂O₃, TiO₂) at temperature of 210-350°C. Sulfation of the catalyst surface is considered to be one of the main causes of decrease of the catalyst activity in the Claus process. According to modern concepts it takes place in the course of the reaction is inevitable because sulfate is a by-product of the Claus reaction on the catalysts of Al₂O₃ and TiO₂. The equilibrium concentration of sulfates on the surface of alumina catalysts amount to 1-3% wt. depending on the temperature and the molar H₂S/SO₂ ratio.

The aim of this work was to examine composition of surface sulfur compounds which are formed in the Claus reaction on the catalyst surface of Al₂O₃ and TiO₂.

The activity tests under Claus reaction conditions were performed in a vertical fixed-bed reactor at temperature of 250°C and space velocities of 2000 h⁻¹. Feed gases with compositions of 3 mole% H₂S, 1.5 mole% SO₂ and 30 mole% H₂O, and balance He, were initially studied. Fraction of the catalyst was 0.1÷0.2 mm. The activity of the catalyst was monitored over a period of 5 h.

Sulfur-containing compounds forming on the catalyst surface during the Claus reaction in the presence of water vapor were extracted by the following procedure. The catalyst sample after the reaction and cooling to room temperature in an inert atmosphere was divided into two specimens. One specimen was put into a 0.1 M solution of KOH, and another was put into a 0.2% solution of zinc acetate. The solutions were evacuated and were kept at vigorous stirring for 30 min. The presence of sulfates, sulfites, thiosulfate and polysulfides was determined in an alkaline solution. For the detection of polythionates we used a weakly acid medium (pH = 5). The content of sulfide, sulfite and thiosulfate in extraction assays was determined by iodometric titration. The presence of sulfate was detected by reaction with barium rodizonat. Semiquantitative determination of polysulfide and qualitative determination polythionates was performed by UV spectroscopy. The contact time of the investigated catalysts and extraction solutions with air did not exceed 30 s during the experiment.

It has been found that sulfite is adsorbed on the surface of both catalysts. Thiosulfate and polythionate are formed in the reaction. Also polysulfide formation is registered on the surface of Al₂O₃. Sulfate was not found in the specimens taken from catalysts immediately after extraction (< 2×10⁻⁶ mol/g). However, in the extraction solutions, which were in contact with air for 5 minutes, was found the presence of sulfate and sulfite was not detected.

It is concluded that the formation of sulfate on the catalyst surface in the Claus reaction in an amount, which leads to catalyst deactivation, is possible only in case of presence of oxygen in the reaction mixture. Sulfate, which is detected in samples of the catalyst after the reaction, is the product of oxidation of sulfite, thiosulfate and polythionates by oxygen.

A mechanism for the conversion of H₂S and SO₂ over alumina and titania is proposed in which surface thiosulfate is formed and reacts with SO₂ and H₂S via a series of oxy-anions to form sulfur and H₂O.
Trimethylolpropane (TMP) is a universal polyalcohol, it is safe and non-toxic product which can be used for producing esters of practical importance. Trimethylolpropane esters are used as lubricants for the aviation industry, and light esters can be used as plasticizers for PVC compositions.

Thermodynamic data for trimethylolpropane esters are absent. Therefore, the database updating on saturated vapor pressures and vaporization enthalpies of these compounds is very important.

The objective of the research is synthesis and determination of saturated vapor pressures and vaporization enthalpies of trimethylolpropane esters.

As objects of research we used synthesized (purity of at least 99.5%) triesters of trimethylolpropane and carboxylic acids C1 - C5 with normal and branched structure: triacetate, tributyrate, trizobutyrate, trivaleriat, trizovaleriat, tripivalates.

Synthesis of TMP esters was performed by azeotropic esterification. The reaction was conducted in the presence of azeotropic agents (benzene or toluene). Concentrated phosphoric acid in an amount of 1% by weight of the reaction mixture was used as a catalyst. For preparation of trimethylolpropane esters the process was carried out with an excess of the appropriate acid, there is a 6:1 mole ratio between acid and trimethylolpropane. The reaction time is 10-15 hours.

The reaction mass was isolated by distillation under vacuum (10-15 mm Hg) with the yield of desired reaction product (with a purity of 98%). Further purification of esters (not less than 99.5%) was carried out on an apparatus for determining the enthalpy of evaporation.

The analysis of esters was carried out on the chromatographic software and hardware complex "Krystall - 2000M" with the following parameters: flame ionization detector (FID), capillary column which DB-1 boned phase, 100 m × 0.2 mm × 0.2 µm; evaporator temperature is 623 K; detector temperature is 573 K; Helium carrier gas, flow division is 1/100.

To determine the saturated vapor pressures and enthalpies of vaporization the transfer method based on the application of the law Clausius - Clapeyron equation was used [1]. On the basis of experimental data we calculated the enthalpies of vaporization of trimethylolpropane esters.

Acknowledgements
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Reference:
SYNTHESIS OF SURFACE OXIDE NANOSTRUCTURES ON THE METALS UNDER ELECTROCHEMICAL TREATMENT IN IONIC LIQUIDS AND THEIR ELECTROCATALYTIC PROPERTIES

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Nanoparticles attract much attention in different fields of science and nanotechnologies due to their excellent physical and chemical properties. Nanoparticles are defined as solid particles of up to 100 nm in size [GOST R 55416-2013]. Active forms of metal oxide nanoparticles that are obtained electrochemically, especially titanium oxide (IV), have a highly-developed surface and can be used as catalyst electrodes. Among various methods of synthesis of metal nanooxides, the synthesis in ionic liquids gets special attention – as promising replacement of traditional solvents. The further development and use of ionic liquids for production of nanomaterials is a future trend for nanotechnologies.

There have been two stages of the research. The first stage consisted of anodic oxidation of titanium and nickel electrodes in the ionic liquid, adding distilled water or propylene glykol. The second stage was the study of electrocatalytic properties of synthesized nanostructures in electrochemical reduction of \( \text{CO}_2 \) in ionic liquids.

At the first stage titanic and nickel catalyst electrodes have been obtained due to the electrochemical treatment; these electrodes have been modified by nanosized particles of titanium oxide (IV) and nickel oxide (II) respectively. For the synthesis of nanostructures of titanium dioxide TiO\(_2\) and nickel oxide NiO the following ionic liquids have been used – on the base of imidazolium cation as electrolyte and stabilizer (bis(trifluorine-methyl sulfonyl)imid 1-butyl-3-methylimidazolium (BmimNTf\(_2\)) and chloride 1-butyl-3-methylimidazolium (BmimCl)). Such ionic liquids are not flammable and also remain stable in a wide temperature range (up to 400°C). They are also characterized by big “windows” of electrochemical stability (from \(-2\) up to \(+2\) V, relative to potential of chloride-silver electrode). At the same time they function as a medium that forms and stabilizes the nanoparticles of metal oxides. Exposure time varied from 1 to 30 minutes, with 1-10 mA DC or constant potential 1-10 V in the air. At the second stage the nanosized titanium and nickel oxides have been studied; these oxides have been synthesized under electro-catalyst conversion \( \text{CO}_2 \) in ionic liquids under various cathode potential and exposure time. Electrochemical behavior of \( \text{CO}_2 \) have been studied in BmimNTf\(_2\) and 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF\(_4\)) ionic liquids. The studied ionic liquids dissolve \( \text{CO}_2 \) well; that was confirmed by the method of cyclic voltammetry. The selected modes have also been tested on the carbon nanotubes (CNTs) in the Ilmenau University of Technology.

As a result of the conducted research the conditions for the one-stage synthesis of applied nanosized structures of nickel and titanium oxides in ionic liquids have been determined. The suggested method allows to obtain the nanoparticles of metal oxides as 0D or 1D structures – depending on synthesis conditions. As a result of electrochemical reduction of \( \text{CO}_2 \) in ionic liquids with anode the light-green sediment forms in the solution out of NiO; based on the data of chemical analysis this sediment corresponds to the insoluble nickel oxalate.
Currently, most products obtained from elastomer materials during vulcanization, which is a chemical crosslinking process space (structuring) and the process of product development of elastomers. An important feature of the elastomeric composite material (rubber) as compared to plastic is that in practice it only exists in the form of finished product with a specific set of predetermined on the step of composition properties.

Industrial production of elastomers - a complex multi-step process characterized by the presence of several stages.

In general, the system of manufacture of products from elastomers is an example of chemical-technological system with series connection of elements.

Production processes include: the preparation of rubber and ingredients; their hanging; in fact, the rubber mixing process with the ingredients, leading to the formation of the intermediate product - crude rubber compound material; structuring process; as well as the control and management of the processes of mixing and structuring elastomeric systems at the stage of the rubber mixture and the finished product.

The needs of the modern world in the products of the elastomers are huge - it's hard to imagine the industry or the national economy, which get along without them.

Currently, the requirements to the level of the properties of products made of elastomers increasingly tougher. To obtain conditioned product with the desired set of properties must be strict adherence to the sequence and parameters of all the preparatory and manufacturing operations, and rubber production stages.

Improving the quality of the finished product contributes to the use of methods of control and management of the processes of mixing and structuring, systematic analysis of production processes and their detailed verbal and mathematical description, as well as information support of decision-making in controlling the processes of mixing and curing based on the analysis rheometer curves and information databases.

Organization Management elastomeric systems structuring process is impossible without the support of its information on the basis of modern information technology and a clear definition of the target pattern.

Leading the pace of demand for means of information support is not equal to the rate of maturity of applied solutions in a constantly changing goals and objectives, which should be based on modern scientific and methodological base, and requires the development of mathematical and algorithmic support on the basis of purposeful information processing.

At the same time the central role played by the processes, techniques and tools of information support products from the production of elastomers. The development of this area traditionally associated with manufacturing plants and aims to increase production efficiency.

For decision-making on sound management and control of mixing and structuring processes elastomeric systems necessary to provide the most complete information about the processes that dictate the need to combine all the available information in the database of information. Solving these problems requires a systematic analysis of the linkages and patterns of functioning and development of objects and processes, taking into account industry-specific information based on database technology, control theory and decision-making.
MODELLING OF PROPERTIES OF LIQUID CRYSTALLINE MATERIALS FOR OPTO-ELECTRONICS

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Liquid crystals (LC) occupy the leading position in opto-electronics. All liquid crystalline materials (LCM) are multi-component mixtures. One of the most important goals for LC material science is to develop low-melting compositions having high clearing temperature, low viscosity and defined dielectric and optical anisotropy.

Thermodynamic analysis of nematic LC systems was hold and the excess thermodynamic functions for mesophase formation were calculated. It was possible to reveal the compensation effect of the excess enthalpy and entropy contributions in binary systems. Analysis showed the considerable deviations from the ideal solution model arise in ternary and quaternary systems. Data for calculations were taken from [1].

Determination of viscosity is very complicated experimental technique for individual LC and LCM. Due to this reason, data on viscosity for LC are rare and erroneous. It is possible to find reliable data for viscosity vs temperature for some tens of the most common LC only [2].

To solve this problem we used the group-contribution scheme. We tested different methods on “model” substances. The methods that gave the best coincidence of literature and experimental data were checked on individual LC and LCM. Literature data were taken from [2, 3]. The best coincidence was obtained using the Orrick–Erbar method: ln(\(\eta/\rho M\)) = A + B/T, where M is molar weight, \(\eta\) is dynamic viscosity, \(\rho\) is density. Coefficients A and B are estimated using the group-contribution scheme. Precision of calculations is enough for engineering goals. Some results are given in a Table.

### Estimation of dynamic viscosity for some common mesogens

<table>
<thead>
<tr>
<th>№</th>
<th>Mesogen</th>
<th>(\eta_{liq}) (mPa·s)</th>
<th>(\eta_{est.}) (mPa·s)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C_5H_11-Ph-Ph-CN</td>
<td>10</td>
<td>13</td>
<td>70 (Is)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28</td>
<td>37</td>
<td>25 (N)</td>
</tr>
<tr>
<td>2</td>
<td>C_5H_11-O-Ph-Ph-CN</td>
<td>12</td>
<td>18</td>
<td>70 (Is)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td>23</td>
<td>50 (N)</td>
</tr>
<tr>
<td>3</td>
<td>C_6H_5-Ph-COO-Ph-OC_6H_{13}</td>
<td>9</td>
<td>6</td>
<td>90 (Is)</td>
</tr>
</tbody>
</table>

References:
UDC 66.023.2:51-74

MODELING OF “CSTR + PARALLEL REACTION $A_1 \leftrightarrow \alpha_{i+1}A_{i+1}$” SYSTEM UNDER PERTURBATION OF REAGENT CONCENTRATION ON INLET

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The correct account of small perturbations and the calculation of local effects [1] are one of the basic problems of development of mathematical and numerical modeling.

The mathematical model is the Cauchy problem for a system of equations of instantaneous balance of concentrations for isothermal continuous stirrer tank reactor (CSTR). In the case of $N$-stage parallel reversible reaction under the action of destabilizing factor $|\Delta c^{\text{inl}}_i| = |c^{\text{inl}}_i - 1| << 1$ of the concentration change the linearized model has the following form

$$\begin{align*}
\frac{d\Delta c_i}{d\tau} + (1 + \sum_{i=1}^N a_i)\Delta c_i &= \Delta c^{\text{inl}}_i(\tau) + \sum_{i=1}^N b_i\Delta \tilde{c}_{i+1} \\
\frac{d\Delta \tilde{c}_{i+1}}{d\tau} + (1 + b_i)\Delta \tilde{c}_{i+1} &= a_i\Delta c_i \\
\tau &= 0, \quad \Delta \tilde{c}_j = 0,
\end{align*}$$

(1)

where $\Delta c_j = c_j - c_{0,j}$, $\Delta \tilde{c}_j = \tilde{c}_j - \tilde{c}_{0,j}$ are the absolute deviations of concentrations $c_j = C_j / C^{\text{inl}}_{01}$ and $\tilde{c}_j = c_j / \alpha_j$ ($\tilde{c}_i \equiv c_i$) from nominal values of $c_{0,j}$, $\tilde{c}_{0,j}$; $\tau = \tau / \tau_0$ is the time in units of the mean time $\tau_0$ of stay of reagents in the apparatus; $C^{\text{inl}}_{01}$ is the nominal concentration of the reagent $A_1$ on CSTR inlet. The indexes denote: $i = 1, N$ is the stage number; $j = 1, N + 1$ is the ingredient number; $0$ is the nominal value; $N \geq 1$ is the number of stages equal to the number of products $A_{i+1}$; $N + 1$ is the number of ingredients.

The dimensionless complexes $a_i \equiv a_{0i} = n_i\tilde{a}_i$, $b_i \equiv b_{0i} = m_i\tilde{b}_i$ play the role of conversion coefficients (CC) of reactions and are equal to the first criteria Damkohler [2]

$$\tilde{a}_i = \bar{K}_{0i(1+i)}c^{n_i}_{0i} \equiv D_{a0i(1+i)}, \quad \tilde{b}_i = \bar{K}_{0i(1+i)}c^{m_i}_{0i} \equiv D_{b0i(1+i)},$$

(2)

where $n_i$, $m_i$, $\bar{K}_{0i(1+i)}$, $\bar{K}_{0i(1+i)}$ are the orders and rate constants of direct and reverse reactions.

It is proved that the stationary mode is practically not violated at high frequencies $\bar{\omega} \equiv \omega \tau_0 >> 1$ of harmonic disturbances $\Delta c^{\text{inl}}_i = E \sin \bar{\omega} \tau$. At low frequencies $\bar{\omega} << 1$, the maximum values of the system coefficients $\xi_{0j} = \Delta c^{\text{out}}_{j\text{max}} / \Delta c^{\text{inl}}_{j\text{max}} = c_0E_j / E$ – as combinations CC of individual elements – are calculated, in particular for two-stage reaction

$$\xi_{01} = B_1B_2 / S, \quad \xi_{02} = a_1B_2 / S, \quad \xi_{03} = B_0a_2 / S \quad [\bar{\omega} \rightarrow +0],$$

(3)

where $B_i = 1 + b_i$ – is the CC of subsystem “CSTR + the $i$-th reaction”; $S = 1 + S^{\text{lin}}_{\text{cons}} + S^{\text{non}}_{\text{cons}}$; $S^{\text{lin}}_{\text{cons}} = \sum a_i + \sum b_i$, $S^{\text{non}}_{\text{cons}} = a_1b_2 + b_1a_2 + b_2b_2$ – is the linear (for formally independent reactions) and nonlinear part of $S$. For CSTR as apparatus $\alpha_{\text{CSTR}} = D_{a\text{CSTR}} = 1$ [2].

1. Lucheyko I.D. The effects of local maximums for AFC of “CSTR + reaction $A_1 \rightarrow \alpha_{i+1}A_{i+1}$” at harmonic perturbations of speed of stream // XV Int. scientific conf. “High-tech in chemical engineering–2014”: abstracts. – Zvenigorod, 2014. – P. 49.

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TEMPERATURE EFFICIENCY COEFFICIENT OF THE “TUBE IN TUBE” HEAT EXCHANGER IN THE COUNTERCURRENT FLOW

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Stationary temperature fields $T_i(l)$ at the concurrent flow of the heat transfer agent (HTA) in the given heat exchanger (HE) have the following form

$$(T'_i - T_i)(T'_i - T'_o)^{-1} = \{1 - \exp[A(\gamma_W - 1)]\} \{1 - \gamma_W \exp[A(\gamma_W - 1)]\}^{-1},$$

$$(T'_2 - T'_2)(T'_1 - T'_2)^{-1} = \gamma_W \{\exp[A(\gamma_W - 1)] - \exp[A(\gamma_W - 1)]\} \{1 - \gamma_W \exp[A(\gamma_W - 1)]\}^{-1},$$

where $0 \leq l = z / L \leq 1$ – is the relative longitudinal coordinate of the HE with length in the flow direction of the hot heat transfer agent (HTA); $T_i(l), T_j(l)$ – are the current temperature values of hot and cold HTA, respectively; $T'_1, T'_2 < T'_o$ – are temperature values of HTA in the tube inlets: $l = 0$ – for hot and $l = 1$ – for cold HTA; $\gamma_W = W_i / W_o = m_i c_i / m_2 c_2$ – is the simplex of flow rate heat capacities (water equivalents) $W_i$, where $m_i$ – is the mass flow rate of HTA, $c_i$ – their specific heat capacity; $A \sim 1 / m_2 c_1$ – is the number of transfer units for cold HTA.

Indexes here and below denote: 1, 2 – outer and inner tube; top stroke – is the beginning ($l = 0$) of HTA; double stroke – is the end ($l = 1$) of HTA (see. fig. 1).

Let’s introduce the temperature heat transfer efficiency coefficient $0 \leq K \leq 1$ according to the formula

$$K = 1 - \frac{T'_1 - T'_o}{T'_1 - T'_o} = 1 - \frac{1 - \gamma_W}{1 - \gamma_W \exp[-A(1 - \gamma_W)]},$$

where $T'_1 < T'_o$ – is the cold HTA temperature at outlet ($l = 0$) of the inner tube.

The logic of formula (2) structure is obvious: $T'_2 = T'_o$ $\Rightarrow$ $K = 0$ – complete absence of heat exchange (in theory this corresponds to condition $\gamma_W = 0 \Leftrightarrow m_1 = 0$), $T'_2 = T'_1$ $\Rightarrow$ $K = 1$ – some “perfect” HE ($\gamma_W \to \infty \Leftrightarrow m_2 \to 0$).

As it follows from fig. 2, even at $A = 1, \gamma_W = 2$ coefficient $K \approx 77\%$. Heat exchange efficiency increases with increasing of $A \sim 1 / m_2 c_2$ at $\gamma_W = \text{const}$, i.e. with simultaneous decreasing of $m_1 c_1$ and $m_2 c_2$ values. The physical reason is the decreasing residence time $\tau_L \sim 1 / m_2$ of the cold HTA in the heat exchange zone. Therefore, the negative side is the reducing of performance $m_2$ (kg/s) of the HE by the heated HTA at $c_2 = \text{const}$. 
Cyclohexanone is one of the most important organic compound; the main part of this product is used for \(\varepsilon\)-caprolactam production in order to get polyamide-6. Experience has proven that the properties of final products are depending directly on amount and type of impurities, which cyclohexanone contains.

Nowadays the technology includes the combined purification system of cyclohexanone, but difficulty of solving of raised problem is that the oxidation product contains low amount of impurities but very wide range of them. It makes the choosing of optimal conditions complicated and does not allow removing the impurities and getting high pure cyclohexanone.

According to literature, one of the most detrimental impurities, which influence the cyclohexanone quality, are aldehydes (eg. butanale, pentanale, hexanale) and unsaturated compounds (eg. cyclohexen-2-one, cyclohexen-2-ol). Line aldehydes are formed as a result of oxidation n-butane, n-pentane and n-hexane, which the crude cyclohexanone contains. Unsaturated cyclic ketones and alcohols are formed in both the cyclohexane oxidation and dehydrogenation of cyclohexanol.

In this investigation, the GC-MS analysis of industrial products of cyclohexanone synthesis was carried out. As the analysis results has shown, that crude cyclohexanone before rectification contains a significant quantity of impurities (approx. 6% by weight, which include compounds with aldehyde and keto-group and unsaturated compounds as well).

As research subjects of kinetic condensation of impurities we have chosen cyclohexen-2-ol as model subject from all the unsaturated impurities and the butyric aldehyde from the aldehyde impurities.

The condensation process of cyclohexen-2-ol with cyclohexanone has been studied. Research suggests that the condensation process of unsaturated impurities carries out effective not with alkali, but with high temperature sulfonic acid ion exchange resins, eg. Amberlyst 70 Dry. The process of butyric aldehyde condensation with cyclohexanone in heterogeneous system with phase transfer catalysts (PTC) trioctylmethylammonium chloride (TOMAC or Aliquat-336) has been studied. It is established, that the presence of PTC allows to increase the reaction rate the condensation process in 2 times. The kinetic of condensation process of butyric aldehyde with cyclohexanone in heterogeneous system with and without PTC was investigated, kinetic equations was obtained.

On the basis of received experimental data are recommended optimal parameters of cyclohexanone purification process, which allow to reduce the amount of impurities and to improve the tradeable caprolactam quality.

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FEATURES OF ALKOXY’S TECHNOLOGY OF THE SYNTHESIS OF OLIGOORGANOSILSESQUIOXANES

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Oligoorganosilsesquioxanes form the basis of polymer composite materials, which are used in various industries. Copolymers are often used to improve properties of the material. One of the main problems in the copolymer production technology by joint hydrolytic polycondensation (GPC) of organochlorosilanes (OCS) with different reactivity (SiCl4>MeSiCl3>PhSiCl3>Me2SiCl2) is formation of separate hydrolysis products. One of the products is often gel. In addition, this technology is characterized by a multistage process, large amounts of waste in the form of HCl, acidic water, and the use of organic solvents. Substitution OCS on organoalkoxysilanes (OAS) is advantageous in the cohydrolysis reactions: the sequence of OAS by reactivity is reversed (Me2Si(OR’)2>MeSi(OR’)3>Si(OR’)4), while the change in the reactivity of a given row is smaller than in the OCS row [1].

It was found [2] that the composition of products of OAS hydrolysis depends on the water and monomer ratios. The hydrolysis of OAS, which is carried out without a solvent or by miscible and non-miscible solvents, has no effect on the composition of the products. This clearly indicates on a kinetic process mode. Water entry in the reaction zone is provided by an increase in its solubility in this region due to the formation during hydrolysis RnSi(OR’)4-n-m(OH)m, homogenization by evolving alcohol.

We take into account these features in synthesis of oligoorganosilsesquioxanes. Couples of monomers (MeSiCl3 and (Me)2SiCl2); (MeSiCl3 and PhSiCl3) are replaced by two pairs (MeSi(OR’)3 and Me2Si(OMe)2); (MeSi(OR’)3 and PhSi(OR’)3) where R’ – Me, Et, i-Pr. Cohydrolysis of monomers is carried out by calculated amount of water (in accordance to M-algorithm) [3] in the presence of acidic and basic catalysts.

Polymethylphenylsilsesquioxanes, polydimethylsilsesquioxanes with high yield in the form of solid resins with desired characteristics are obtained.

Specific examples of oligoorganosilsesquioxanes synthesis of various compositions are presented in the report.

This study is of practical interest for its subsequent industrial application.

References:
Bifluoride processes in applied chemistry have proven themselves as highly effective, closed technologic circuits and meet environmental conditions. Baddeleyite-gelzircon concentrate of Algama ore deposit (Khabarovskiy Kray) was one of the first objects for chemical processing with ammonium bifluoride for the first time in the mid-1990’s.

A major unique research project was completed in the Institute of Chemistry of DVO FEB RAS. Unusual concentrate showed surprising chemical activity. The interaction between concentrate and NH₄HF₂ started at ambient temperature. Reaction in general is described in the following way:

\[ \text{EO}_2 + 3.5 \text{NH}_4\text{HF}_2 = (\text{NH}_4)_3\text{EF}_7 + 0.5 \text{NH}_3 \uparrow + 2 \text{H}_2\text{O} \uparrow. \]

The main reason of high concentrate reactivity is the presence of rare mineral gelzircon \([\text{Ca,Fe}]\text{Zr}_5\text{Si}_4\text{O}_{19} \cdot 2\text{H}_2\text{O}\) which dramatically contrast with normal low-reactive zircon.

In order to verification of bifluoride method the pilot batch of concentrate weight of 300 kg was processed to high purity end products. At the first stage large amounts (360 kg) of \((\text{NH}_4)_2\text{SiF}_6\) with a purity level of 99.998 % were produced from the resulting mixture of fluorammonium salts by sublimation at 350°C. The fluoride residue mainly composed of \(\text{ZrF}_4\) after little complementary processing with \(\text{NH}_4\text{F}\) was sublimated at 960°C and converted into \(\text{ZrO}_2\). Target products (high purity \(\text{ZrF}_4\) and \(\text{ZrO}_2\)) as well as \(\text{SiO}_2\) were free from radiation. Radioactive elements contained in this ore were concentrated into small fixed fluorceramics during \(\text{ZrF}_4\) stripping. Subsequent researches with ilmenite \(\text{FeTiO}_3\), scheelite \(\text{CaWO}_4\) and other ores were also successfully.

But there are some types of chemically resistant mineral raw materials which almost did not react with \(\text{NH}_4\text{HF}_2\). These include zircon \(\text{ZrSiO}_4\), rutile \(\text{TiO}_2\), cassiterite \(\text{SnO}_2\) and others. Zircon is more common zirconium industrial mineral having its own fields and occurring among heavy sands along with rutile, ilmenite, monazite, cassiterite and magnetite. Zircon refers to the persistent minerals. It turned out that \(\text{ZrSiO}_4\) contained in the Algama ores also (7.5 %). That’s why it was important to find a way to decompose of \(\text{ZrSiO}_4\) and minerals like him with \(\text{NH}_4\text{HF}_2\). We designed closed-type one liter fluoroplastic (PTFE) reactor embedded into steel jacket for chemical decomposition of refractory minerals (zircon, rutile and cassiterite) with \(\text{NH}_4\text{HF}_2\) reinforced HF. In particular 100 g of Algama concentrate contained of \(\text{ZrSiO}_4\) was fluorinated to soluble forms of main components for 5 h at 170°C. The Zr conversion was 97.6 %. Ammonium oxofluorozirconates look like white wet neutral paste (owing to emission of water in the course of reaction) with pH 7. It was important that ammonia vapors did not release as usually. Unlike described fluorination reactions accompanied by release of \(\text{NH}_3\) and \(\text{H}_2\text{O}\) these processes proceeded according to equations:

\[ \text{ZrSiO}_4 + 6 \text{NH}_4\text{HF}_2 + 2 \text{HF} = (\text{NH}_4)_3\text{ZrF}_7 + (\text{NH}_4)_3\text{SiF}_7 + 4 \text{H}_2\text{O}. \]

The released water remained in closed reactor that facilitated solid-phase reaction and provided its completeness. The cooled product was extracted from apparatus quite easily. Zirconium hydroxide (or other hydroxides) can be received from \((\text{NH}_4)_2\text{ZrF}_7\) with ammonia after partial evaporation of aqueous solutions owing to salting-out effect of \((\text{NH}_4)_3\text{SiF}_7\). All radionuclides after concentrate decomposition with \(\text{NH}_4\text{HF}_2\) remained in insoluble residue.
RADIOACTIVE ELEMENT BEHAVIOR IN BIFLUORIDE PROCESSES

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State-of-the-art technology relating to mineral raw materials may be discussed on the assumption of radioactive elements problem solving. It means concentration and separation of hazardous constituents at an early stage of technological chain. Unfortunately many rare metal ores which satisfactory react with ammonium hydrodifluoride relate to radioactive natural raw materials. Algama zirconium ores are exactly such ones.

The sublimation of (NH₄)₂SiF₆ and ZrF₄ at different temperatures from fluorinated concentrate was accompanied by spontaneous fixation of natural radionuclides in fluoride zirconium matrix as fluorceramics. The activity of fixed residue resulted in 30-fold increase. However for other types of radioactive raw mineral materials from list of “bifluoride technologies” the sublimation stage is not convenient or impossible if volatile fluorinated products are not formed, for example, monazite Ce(La)PO₄ or if technology is not “dry”. In such cases the task of fluorinated radionuclides separation can be achieved another way.

When investing the decomposition of concentrates with NH₄HF₂ insoluble radioactive portions were founded. Due to this finding radioactive impurities can be collected on the filter during filtration procedure of aqueous leaching solution, i.e. at the start of process string.

Gamma-spectrometry analysis performed on Algama sample showed that according to integrated activity of ²²⁶Ra, ²²⁸Ra, ²²⁴Ra, ²³²Th, ⁴⁰K and ¹³⁷Cs untreated concentrate and insoluble residue on the filter may be classified as hazardous Class IV but target product (ZrO₂) as I (without limit on radiation hazard). As whole uranium behavior in bifluoride processes is optimal for technology. The fluorination of U₃O₈ with NH₄HF₂ proceeds with formation of soluble (NH₄)₃UO₂F₅ and insoluble NH₄UF₅. Radium forms insoluble RaF₂.

\[
\begin{align*}
U₃O₈ + 7.5 NH₄HF₂ & = 2 (NH₄)₃UO₂F₅ + NH₄UF₅ + 0.5 NH₃ + 4 H₂O \\
RaO + 2 HF & = RaF₂ + H₂O
\end{align*}
\]

Most of uranium (94.1 %) converted into UO₂²⁺ that allows to using anion-exchange resins for its concentration and extraction. Another way consists of its preliminary separation at low pH. Chemical precipitation of uranium occurs from moderately evaporated filtrate almost with ammonia at neutral medium after removal of mentioned above radioactive part of concentrate in the form of bright yellow ammonium diuranate (NH₄)₂U₂O₇ {so-called “yellowcake” or (NH₄)₂U₂O₇}. This approach was obligated to a great difference in pH of ammonia deposition between (NH₄)₂U₂O₇ (pH 7.2-8.0) and Zr(OH)₄ (pH 9-12).

\[
2 (NH₄)₃UO₂F₅ + 6 NH₃⋅H₂O = (NH₄)₂U₂O₇↓ + 10 NH₄F + 3 H₂O
\]

Monazite reacts with NH₄HF₂ in a complicated manner. Cerium as well as other lanthanides forms insoluble salt.

CePO₄ + 2 NH₄HF₂ + 2HF = NH₄CeF₄ + NH₄PO₂F₂ + 2 H₂O

In additional to insolubility of NH₄CeF₄ and other NH₄LnF₄ all LnF₃ have very low vapor pressure and so they are reputed as nonvolatile. The mixture of insoluble fluorides NH₄LnF₄ and RaF₂ can be isolated from each other by boiling HCl with backflow condenser. Lanthanides converted into soluble chlorides. Previously NH₄LnF should be annealed in order to recycling of NH₄HF₂. As we have seen time and again bifluoride technology is multivariate tool for solution of many traditionally difficult chemical problems.
CATALYTIC HYDROGENATION OF CARBOXILIC ACIDS AS A METHOD OF PRODUCTION OF HIGHER ALCOHOLS

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Last years there is a great interest to the production of biofuels as an alternative of fossil fuels. This is due to the following reasons:
- ecological problems related to the climate changes;
- an increase of petroleum prices;
- energy source diversification [1].

There are different methods of biofuel production. One of them is transesterification of oils and fats to fatty acid methyl and ethyl esters [2]. However the fuel obtained by such method has many disadvantages, e.g. ambiguous economical efficiency due to the use of eatable oils and low quality due to the presence of large amount of non-saturated compounds [3]. Nowadays the interest of researchers is focused on the modification of common biodiesel with use of different technologies involving the use of catalysts on the base of transition metals (Ni, Pt, Pd, Ru etc.) [4]. One of these methods is the production of biofuel in the form of saturated hydrocarbons or fatty alcohols.

One of the common methods of fatty alcohols production is hydrogenation of fatty acids and their derivatives. Last decades the investigation focused on the improvement of catalytic systems used in the selective hydrogenation process to increase the productive capacity and decrease the material and energy costs are developed.

In this work the process of liquid-phase hydrogenation of stearic acid in the medium of non-polar solvents – hexane, dodecane, cyclohexane and toluene – is studied. The process was carried out at the following conditions: temperature – 100 °C, hydrogen partial pressure – 3 MPa, initial stearic acid concentration – 1 mol/L, catalyst mass – 0.1 g. Pd-containing catalysts supported on activated carbon and hypercrosslinked polystyrene (HPS) were used. The liquid phase analysis was performed using GC-MS. The process effectiveness was estimated basing on stearic acid conversion as well as the selectivity regarding to stearyl alcohol.

The sample analysis showed that the main reaction products were stearic aldehyde, stearyl alcohol and n-octadecane. Since the reaction was performed without any catalyst the main product was found to be stearic aldehyde due to a partial reduction of carboxylic group of stearic acid. While using dodecane it was founded that the main reaction product was also stearic aldehyde that may be connected with a high density of the solvent. The use of cyclohexane as a solvent leads to the formation of large amount of hydrocarbon indicating the full carboxylic group reduction in all series of the experiments. The highest yields of alcohol (98 and 99% respectively) were obtained in the cases of using of hexane and toluene in the presence of Pd/HPS catalysts.

References:
THE USE OF HEAT PUMPS IN CONDUCTING COMBINED AND ASSOCIATED MASS TRANSFER PROCESSES

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As it is known, various mass transfer processes are used for separation and purification of substances from the impurities (absorption, distillation, rectification, extraction, crystallization, etc.). Each of them has its own area of technologically possible and economically expedient use. Often restrictions on the use of one or another process is due to the physico-chemical properties of separated mixtures and to the presence of singular points at the phase equilibrium diagram (azeotropic, eutectic, etc.). The boundaries of the possible separation can be significantly extended when using a combination of several mass transfer processes. However, the use of such conjugate separation methods are often associated with significant energy costs, due to the need for heating and cooling of streams of separated mixtures during their transfer from one stage of separation to another.

The use of heat pumps in the stages of regenerative heat exchange between input, withdrawn and recirculating streams can significantly reduce the cost of thermal energy. Considering this, we have analyzed the use of compressive heat pumps of open and closed types in the separation of a number of binary mixtures by a combination of distillation, rectification and fractional melting with a fractional crystallization process. At the same time, the different options for this separation have been proposed and analyzed. As a result of the research it was shown that the application of heat pumps in all these processes can significantly reduce (sometimes several times) the energy costs of the separation processes.

Heat pumps can also be used during the combined processes. As part of this work we have carried out the analysis of heat pumps application efficiency in the processes of evaporation and vacuum evaporation crystallization. In carrying out the evaporation crystallization secondary compressed vapors can be used to heat the crystallizer, and in the case of vacuum evaporation crystallization secondary pairs can be used for heating of initial solutions or for their pre-evaporation before throttling. As a result of our studies the influence of main process parameters (temperature, pressure, compression ratio of the secondary vapor, etc.) on the energy efficiency of the processes studied has been found. A number of options for their implementation has been considered. It is shown that the use of the heat pump during combined processes also can significantly reduce the energy costs for their realization.
Hydrogen peroxide is widely used in large production and in the laboratory [1], because of a number of valuable properties: low cost, large scale production and many opportunities to use. All current research in the field of hydrogen peroxide may be divided into three groups: preparation, use and maintenance. Among three directions of the stabilization study develops lowest rate, while the problem of maintaining hydrogen peroxide is one of the key. It is known that when stored under the action of elevated temperatures, light, impurities, and organic salts of transition metal impurities hydrogen peroxide is destroyed [2]. To avoid that the solutions adopted to introduce stabilizers - substances which increase the peroxide during storage due to possible breakage collapse paths in a system. Generally known stabilizers may be divided into two groups: organic and inorganic. High demand for hydrogen peroxide and the diversity of its application pathways give to researchers the task of finding new compounds to expand the existing range of stabilizers allowing improving the properties of peroxide.

Conducting research on synthesis of organic peroxide from carbonyl connections and hydrogen peroxide was detected that aryl alkyl ketones effectively stabilize water solutions of hydrogen peroxide. Further it was prepared the series of compositions with additives from the class aryl alkyl ketones. Two groups were formed: stabilizing and destabilizing additives. It revealed that the best stabilizing substance was acetophenone.

Literature analysis in the hydrogen peroxide stabilization mechanism area [3] allows us to formulate a number of hypotheses about action mechanism of stabilizing additives:
1. Stabilizer connects the catalyst particles;
2. Stabilizer breaks possible pathways of disintegration;
3. Activity of stabilizer connects with UV absorption;
4. «Secondary» stabilizing effect takes place in this system

Thus, it is proved that acetophenone has the best stabilizing properties among the investigated compounds from the class of aryl alkyl ketones. Some hypotheses regarding the mechanism of stabilizing action also investigated and held their discrimination.

Acknowledgements
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References:
KINETICS OF GLYCIDOL OBTAINING BY ALLYL ALCOHOL EPOXIDATION WITH HYDROGEN PEROXIDE AT ZEOLITE CATALYST (TS-1)


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The glycidol and other epoxides (ethylene oxide, propylene oxide, epichlorohydrin, etc.) are important intermediate products of basic and fine organic synthesis. One of the methods for glycidol producing is liquid-phase epoxidation of allyl alcohol by hydrogen peroxide on titanium-containing zeolite catalyst TS-1. Deterrent to the use of this catalyst in industrial scale has been the lack of granular form. Recent work [1] aimed at obtaining a granular form of the catalyst, exhibiting high activity and selectivity in the epoxidation processes, remove this restriction. Therefore, of particular practical importance are kinetics studies of this process.

\[
\text{OH} 
\begin{array}{c}
\text{H}_2\text{O}_2, \text{cat. TiO}_2\text{SiO}_2(\text{TS-1}) \\
\text{CH}_3\text{OH}, 20-50^\circ\text{C}, 3\text{h}
\end{array} 
\]

Together with the main reaction (glycerol formation) there are a number of side reactions in the system leading to form such byproducts as glycerin, 1-methoxypropane-2, 3-diol and minor amounts of other substances:

\[
\text{O} 
\begin{array}{c}
\text{OH} \\
\text{H}_2\text{O}
\end{array} 
\]

\[
\text{O} 
\begin{array}{c}
\text{OH} \\
\text{CH}_3\text{OH}
\end{array} 
\]

In addition, the reaction products contain oxygen, which is formed by the reaction:

\[
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2
\]

The factor of limiting the use of TS-1 catalyst on a industrial scale was the lack of a granular form. Recent research [1], aimed at obtaining the granular form of the catalyst exhibiting high activity and selectivity in epoxidation processes, this restriction is removed, and thus have a particular practical importance of studying the kinetics of the process. Based on the literature data [2] proposed several structural kinetic models. The results of the univariate experiments series determined the optimal model parameters that best describe experimental data. Hypotheses discrimination made on statistical criteria. To confirm the working hypotheses were conducted additional experiments.

Acknowledgements

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References:

THE EQUILIBRIUM OF COMPLEXATION IN PdBr₂-LiBr-THF SYSTEM

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Palladium complexes are basis of the catalytic systems widely used in organic synthesis. [1] These systems exhibit a wide range of catalytic properties in reactions involving carbon monoxide and other substrates (alkynes, alkenes, dienes, arenes, alcohols, phenols, amines) [2]. Valuable products of organic synthesis: carboxylic acids, carboxylic acid anhydrides, esters, amides, lactones, and others are products of these processes [2]. The coupled processes can be proceed in such systems too [3].

The oxidation of carbon monoxide (I) coupled with carboxylation of alkenes into carboxylic acids (II) proceeds in the PdBr₂-CuBr₂-THF-H₂O system at 30°C and atmospheric pressure of a mixture of oxygen and carbon monoxide [4, 5].

\[
\begin{align*}
\text{CO} + 0.5 \text{O}_2 & = \text{CO}_2 \quad (I) \\
\text{RCH} = & \text{CH}_2 + \text{CO} + \text{H}_2\text{O} = \text{RCH(COOH)CH}_3 + \text{RCH}_2\text{CH}_2\text{COOH} \quad (II)
\end{align*}
\]

Kinetics of this process was studied earlier [4, 5], but the lack of information on the distribution of palladium complexes in the catalytic system didn’t allow to propose the detailed mechanism of this process. In this connection, the main aim of this work is to study the equilibrium of complexation in PdBr₂ – LiBr – THF system. The obtained information allowed to determine palladium complexes which dominate in the original catalytic system (PdBr₂ - CuBr₂ – THF) used for hydrocarboxylation alkenes.

The study of solutions was carried out by electron spectroscopy method using a spectrophotometer Specord M-40. The spectra were recorded with respect to the solvent (tetrahydrofuran) at a temperature of 23 ± 2°C in quartz cuvettes (thickness of 0.01 cm and 0.5 cm). The mathematical treatment of the received data was carried out using hypotheses including the formation of monomeric and dimeric palladium complexes. The equilibrium constants of complexation stages of monomers and dimers as well as the extinction coefficients of palladium complexes were calculated.

The comparison of the mean-square error description of the results of experiments for the models showed that the model taking into account the formation of four monomeric (PdBr⁺, PdBr₂, PdBr₃⁻, PdBr₄⁻²⁻) and three dimeric (Pd₂Br₂²⁺, Pd₂Br₄, Pd₂Br₆²⁻) complexes is the best model for describing the experimental data. In the frames of this model, we calculated spectra of the individual monomeric and dimeric complexes of palladium.

Acknowledgements
This investigation was supported by the Russian Foundation for Basic research (grants № 16-33-00371 and № 14-03-00052).

References:
Methanol is one of the most important products of organic synthesis and it ranks among leading organic products in the terms of production. It is mainly manufactured in the industry from synthesis gas by producing a mixture of crude methanol. The main byproducts are dimethyl ether (DME) and water. Other components (mainly C₂-C₆ alcohols, ethers, and some saturated hydrocarbons) have traced concentrations and their overall concentration usually does not exceed 1 wt. % [1]. Propanol is found in the largest quantity among other alcohols. Therefore it was chosen as a representative of the class of alcohols, and in the designed experiment it simulates the whole class of these compounds. Pentane has been selected by the same principle. Thus, the following simplified structure of crude methanol has been adopted [1]: DME – 0.25% of wt.; pentane – 0.10% of wt.; methanol – 89.10% of wt.; propanol – 0.13% of wt.; water – 10.42% of wt.

Models NRTL, NRTL-RK, and UNIQUAC-RK were selected for consideration to simulate phase equilibria on the base of recommendations of the authors [2]. As a result, it was found by the checking of adequacy of vapor-liquid equilibrium description, that the UNIQUAC-RK model is the least erratic in describing the experimental data.

The selected model allowed to simulate the considered multicomponent mixture and to obtain its phase diagram. The projection of a pentatope and its flat map are given in Fig. 1. It was found that the mixture has a number of areas of delamination and separatrix varieties.

References:
The behavior of an electron in a molecule is described by the Hamiltonian operator, containing both single-particle and two-particle components. Near the nucleus, where \(|r_i - r_j| >> r_i\), it can be assumed that the electron correlation is so small that it can be neglected. Valence electrons of Van der Waals system are too far from the each centers, that is why, this system is divided into two subsystems. One of them is located near the nucleus and it is described by the sum of single-particle operators. Average values of this sum of operators are characterized by single-particle density matrix. Another subsystem that is equidistant from each monomer of loosely coupled system is described by the sum of two-particle operators. It is characterized by the two-particle density matrix. N-representability problem is not resolved for the two-particle density matrix. For this reason it is impossible to directly use it for research loosely coupled systems. This problem can be solved by using both an explicitly correlated approach F12 and an approach where the use of bond functions. Later approach have the same accuracy as approach F12, but requires less computational power. Calculations show that the use of bond functions gives accurate results with small basis sets in the case of inert-gas dimers. In this paper, to solve the problem described above one was chosen the approach at that basis set with bond functions is used because it is the most optimal approach. (CCl₄)$_2$, (CBr₄)$_2$ и (Cl₄)$_2$ were chosen as objects of research. Symmetry Td of monomers are fixed, geometries of this monomers have been optimized by CCSD(T)/aug-cc-pVQZ using effective core pseudo potentials 10SDF, 28MWB, 46MWB for CCl₄, CBr₄ and Cl₄, respectively. It allowed to establish the values of R(C-Cl)=1.75, R(C-Br)=1.94, R(Cl)=2.1 angstrom. The second part of the work consisted of the construction of sections of the potential energy surface of dimers along the bond C-C in the approximation of hard monomers for the most stable configuration D3d by CCSD(T) using the pseudo potentials for the basis sets cc-pVNZ and aug-cc-pVNZ (N = D, T) both with a test set of bond functions \{33221\} and without them. Analysis of the results showed the following: when the section of the PES was built without using the basis set with bond functions, the interaction energy \(D_e\) between monomers in dimers (CCl₄)$_2$, (CBr₄)$_2$, (Cl₄)$_2$ takes the value from 0.56 to 2.6 kcal/mol, from 0.05 to 3.56 kcal/mol from 0.65 to 3.85 kcal/mol in the case of the use of bond functions, \(D_e\) ranged from 1.88 to 2.89 kcal/mol, and from 2.52 to 4.01 kcal/mol from 1.43 to 4.11 kcal/mol, respectively. Based on these data one can conclude that the use of basis sets containing bond functions allows to get more accurate results using a small basis set. At first time this approach also allowed to estimate the energy of interaction between molecules Cl₄. Furthermore it was important to choose a appropriate core affective pseudo potential. That is why, sections of PES for dimer (CCl₄)$_2$ were built by methods MP2/cc-pVXZ and MP2/aug-cc-pVXZ (X=D, T) for core affective pseudo potentials 10SDF, 10MWB, LAN, CRENBL, CBKJC and case of full electron set. Distinction energy interaction \(D_e\) for the different sections of PES (CCl₄)$_2$ were small and amounted to no more than 0.1 kcal/mol. This fact permits to state that mainly valency electrons participate in formation of intermolecular interactions. These is one of evidence that the valency electrons are concerned with the two-particle density matrix.
GENERALIZED DEPENDENCES OF VARIOUS PROPERTIES OF ALCOHOLS

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To construct a generalized dependency must be selected scale for the unknown quantities and variables. These scale states of points are located in P-V-T (pressure-volume-temperature) space.

The scale of the construction of generalized dependences the studied properties and variables of the problem must be sustainable. And to find a sustainable transition from liquid to vapor is investigated the behavior of characteristic function of the free energy. Since the phase transition occurs at a constant temperature, the free energy is equal to the work of expansion. In the analysis of the transition of the liquid-vapor, on curve of dependence work of expansion from temperature for all investigated substances passes through a maximum. The temperature corresponding to the maximum expansion work is denoted by $T_m$. It was noted that the temperature $T_m$ associated with $T_c$ (critical) with the simple relation ($T_m = 0.76T_c$) with a spread of 2%. Naturally, this state corresponds to the free energy minimum value and in accordance with the principle of minimality of characteristic functions of this process is stable. Therefore, the parameters of this process are chosen as the bringing scale in the construction of dimensionless dependencies.

All physical properties of materials at the phase transition liquid-vapor are closely linked. It should be noted that from value of the dimensionless density $\frac{\Delta \rho}{\Delta \rho_m}$ depends dimensionless quantities such as entropy $\frac{\Delta s}{\Delta s_m}$, enthalpy of vaporization $\frac{\Delta H}{\Delta H_m}$, surface tension $\frac{\sigma}{\sigma_m}$ etc.

The present work is devoted to the study of these connections for primary alcohols. Because this class of organic compounds widely used in the chemical industry, but the experimental data on the enthalpy of vaporization is too small. Processing carried out by known experimental data for the following compounds: methanol, ethanol, propanol, butanol, 2-butanol, pentanol, 2-pentanol.

$$\frac{\Delta H}{\Delta H_m} = -0.098 \left( \frac{1 - \tau}{1 - \tau_m} \right)^2 + 0.675 \frac{1 - \tau}{1 - \tau_m} + 0.434$$  (1)

The error values calculated by formula (1) compared with the experimental data does not exceed 4%.

To confirm the existence of links between the different properties of substances at the phase transition liquid-vapor were compared to the given values enthalpy of vaporization and surface tension. The relationship between $\frac{\Delta H}{\Delta H_m}$ and $\frac{\sigma}{\sigma_m}$ showed reasonably good match existing experimental data of various authors. Approximation of the results given a formula that has the following form:

$$\frac{\Delta H}{\Delta H_m} = -0.099 \left( \frac{\sigma}{\sigma_m} \right)^2 + 0.697 \frac{\sigma}{\sigma_m} + 0.416$$  (2)

The error does not exceed 3% for the following compounds: methanol, propanol, butanol, pentanol.
ACCOUNTING OF FEATURES OF THREE-LIQUID PHASE EQUILIBRIA IN CALCULATING THE MATERIAL BALANCE OF SEPARATION FLOWSHEETS FOR N-HEXANE – CYCLOHEXANE – FURFURAL – WATER MIXTURE

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This paper studies calculation of material balance of separation schemes for n-hexane (1) - cyclohexane (2) - furfural (3) - water (4) mixture characterized by the presence of three-liquid phase equilibria region. Separation flowsheets include systems based on a combination of distillation and spontaneous delamination (Fig. 1) and a different application of the first (1a) or second (1b) given separation in the first separation column, and the phenomenon of delamination at the first separation stage (1c).

An important element in the separation flowsheets is decanter which contains three liquid phases. Two liquid layers (water layer and furfural layer) can be separate on stripper column to recovery water and furfural. Features of the material balance calculation are related with the recovery of hexane and cyclohexane from the hydrocarbon layer. Here, important is the ratio n-hexane and cyclohexane concentration ($X_1/X_2$) in the hydrocarbon layer and in the initial mixture. To simplify and accelerate of the material balance calculation of separation flowsheets for separating mixtures of different composition are proposed to find the point of intersection of two lines corresponding to an equal ratio of $X_1/X_2$ in the initial mixture and in the hydrocarbon layer. We accept linear change of ratio $X_1/X_2$ in the hydrocarbon layer, which is consistent with the computing experiment. Then based on the conditions of a liquid-liquid-liquid phase equilibrium we can find compositions and the amount of furfural and water layers that will be correspond decision of the material balance of the separation scheme of the initial mixture.

Calculation of phase equilibrium liquid-vapor, liquid-liquid-liquid is produced by AspenPlus 7.3 software using NRTL equation. Distillation columns operate at a pressure of 101.3 kPa. Decanters operate at 20 °C. 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. For equimolar composition of the initial mixture are showed the energy benefits of separation flowsheet 1c equal 7.8% (18%) compared with the flowsheets 1a (1b).

Acknowledgements
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KINETIC ASPECTS OF THE INFLUENCE OF Co PRESSURE ON THE HYDROCARBOMETHOXYLATION OF CYCLOHEXENE CATALYZED BY PALLADIUM-DIPHOSPHINE SYSTEM

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Hydrocarbalkoxylation is a method of insertion of the ester function to the different unsaturated structures. The reaction catalyzed by the palladium-diphosphine systems flows in the mild conditions. However, the studies of hydrocarbalkoxylation are embarrassed in the multicomponent systems which includes three reagents (alkene, alcohol and CO) and three components of catalytic system (palladium precursor, phosphine and acid promotors). In this connection the reaction of cyclohexene hydrocarbomethoxylation which allows to formation of a single product (methyl cyclohexanecarboxylate) was chosen as the model object. In the last years diphosphinic compounds were established more active promotors of palladium catalysts then monophosphinic, therefore, the Pd(OAc)₂ / trans-2,3-bis(diphenylphosphinomethyl)norbormane (TBDPN) / p-toluenesulphonic acid (TsOH) system was used as a catalyst.

Trans-2,3-bis(diphenylphosphinomethyl)norbormane was synthesized as described previously in [1]. The investigations were studied in a jacketed batch reactor equipped with a sampler. Each experiment was performed in toluene at a necessary constant temperature and CO pressure. During the kinetic experiments, the reaction mixture was sampled at specific time intervals, and the samples were analyzed by gas-liquid chromatography.

In the 358 - 378 К temperature range the effect of CO pressure on the reaction rate was studied. It was found that dependences of reaction rate correlated with CO pressure with maximums in the range of 2-3 MPa and the reaction rate increased with the temperature enhance from 358 to 373 K. At 373 and 378 K the reaction rate was practically identic. The reaction rates at the maximums were about twice as much as the rates at the maximums at catalysis by the Pd(OAc)₂ / PPh₃ / TsOH system and about four times as much as the rates in the presence of Pd(PPh₃)₂Cl₂ / PPh₃ / TsOH catalytic system, which were used earlier. The results were interpreted via a hydride mechanism including diphosphine-palladium complexes as intermediates, augmented with ligand exchange reactions, which lower palladium catalyst activity. The experimental data were established corresponding to the kinetic equation in the 358-378 K temperature range. The obtained values for effective constants of action are satisfactorily described by the Arrhenius equation on the 358-373 K temperature range. Probably arranged temperature dependence is connected with a complication of reaction mechanism and thermic unstability of palladium complexes. On the base of received results, temperature of 373 K and CO pressure of 2 MPa were established optimal for increase of reaction rate in the presence of diphosphine-palladium catalytic system.

Acknowledgements
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Reference:
UDC 66.091.2

KINETICS OF THE CATALYTIC OXIDATIVE CHLORINATION OF METHANE

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Oxidative chlorination of methane (1) is the first stage of the chlorine balanced process of the light olefins production via methyl chloride pyrolysis (2):

\[ \text{CH}_4 + \text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O} \ (1), \]

\[ n \text{CH}_3\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 + \text{C}_4\text{H}_8 + \text{other hydrocarbons} + n \text{HCl} \ (2). \]

The first stage, which is carried out in the gas phase (temperature range is 300-420°C, catalyst – CuCl2-KCl-LaCl3/Al2O3-SiO2 with a specific surface area of up to 27 m²/g), to obtain methyl chloride has been studied.

It was found by TEM and PFA methods that copper and potassium chlorides are unevenly distributed on the surface of the support, forming agglomerates with high content of salts, including double chlorides, such as KCuCl3, K2CuCl3 or K2CuCl4, hydrate K2CuCl4*2H2O and hydrochlorides Cu3Cl4(OH)2 and Cu2Cl(OH)3. Lanthanum is distributed more evenly.

Using the software package “Kinetic”, empirical rate constants and formal orders according to partial pressures of reagents were assessed for four power equations, which describe the rate of methyl chloride formation (table)

<table>
<thead>
<tr>
<th>Kinetic equation</th>
<th>The observed rate constant ( \text{mol/l·h·atm} )</th>
<th>Standard deviation, %</th>
<th>Correlation index</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ r = k \cdot O_2^{0.18} \cdot CH_4^{1.12} \cdot HCl^{0.007} ]</td>
<td>14.62</td>
<td>12.56</td>
<td>0.868</td>
</tr>
<tr>
<td>[ r = k \cdot O_2^2 \cdot CH_4^{1.19} \cdot HCl^{0.047} \cdot Cl_2^{0.27} ]</td>
<td>58.34</td>
<td>11.29</td>
<td>0.897</td>
</tr>
<tr>
<td>[ r = k \cdot O_2^0 \cdot CH_4^{0.775} \cdot HCl^{0.006} \cdot H_2O^{0.638} ]</td>
<td>24.3</td>
<td>7.52</td>
<td>0.959</td>
</tr>
<tr>
<td>[ r = k \cdot O_2^0 \cdot CH_4^{0.769} \cdot HCl^{0.007} \cdot Cl_2^0 \cdot H_2O^{0.641} ]</td>
<td>24.67</td>
<td>7.41</td>
<td>0.960</td>
</tr>
</tbody>
</table>

The comparison of four equations (table 1) shows that the last equation in the table, that takes into account the concentration of all initial reagents and water, as well as chlorine, describes the experimental data most accurately. It should be also noted that the increase of water concentration significantly speeds up the oxidative chlorination of methane (H2O0.64), which is comparable to the degree of influence of methane (ranging from 0.77 to 1.19, depending on the hypothesis). The partial pressure of oxygen and one of chlorine do not affect the rate of methyl chloride formation, in all power equations. The impact of the partial pressure of hydrogen chloride is negligible. Thus, it is not advisable to exclude concentration of water and methane from kinetic power models. The influence of by-products (methylene chloride, chloroform, carbon tetrachloride and deep methane oxidation products) was not taken into account, because the selectivity of the process to methyl chloride formation was over 97% (under not-kinetic conditions the selectivity was more than 90%). Consequently, by-products, except water, formed primarily in the reaction of the Deacon, and were almost absent in the system.
Liquid crystals (LC) are the key materials for modern optoelectronic devices. Stable and reproducible properties of industrial mixtures depend on purity of individual mesogens. The intermolecular interactions type in the LC – non-mesogen system is a basis for the solvent selection for purification of the individual components by crystallization. Thermodynamic models based on the Hildebrand and Hansen solubility parameters, Flory-Huggins equation can be used to predict the phase diagram type and to estimate the liquidus curves. Homologous LC p-alkyloxyphenyl-p’-alkyloxybenzoates – non-mesogen systems were investigated by the thermal analysis and solubilities methods. Solubility curves of mesogens in solvents of different polarity (n-alkanes, cyclohexane, aromatics, chlorinated alkanes, alcohols, esters, acetone, acetonitrile) were obtained. The simple method based on the Hansen [1] solubility parameter estimation scheme was proposed. Figure 1 shows the relationship between solubility ($X_1$) of LC ($\text{C}_4\text{H}_9\text{O}-\text{C}_6\text{H}_4\text{COO-C}_6\text{H}_4\text{OC}_6\text{H}_{13}$) and radius ($R_a$), which is calculated via the differences between the contributions of dispersion ($\delta_d$), polar interactions ($\delta_p$) and hydrogen bonding ($\delta_h$) of the solubility parameters. For LC it is also confirmed that at increasing $R_a$, solubility decreasing. The proposed method can be used for the express technique of the solvent selection for purification of mesogens and for mutual miscibility of components.

$$R_a^2 = 4(\delta_d - \delta_d)^2 + (\delta_p - \delta_p)^2 + (\delta_h - \delta_h)^2$$

**Reference:**
“Guest-host” effect (GHE) is the oldest and the most interesting electro-optical effect for a practical usage in liquid crystalline displays. GHE is based on the light absorption anisotropy of dichroic dyes in nematic liquid crystalline matrix. Majority of industrial dichroic dopants have the different structures in a comparison with nematic liquid crystals (LC) and low solubilities accordingly. Differences in melting temperatures of components lead to the phase diagrams with the boundary nematic solutions [1]. The estimation of the liquidus curves in LC – dye systems is the promising goal.

Thermodynamic models based on the Hildebrand and Hansen solubility parameters, Flory-Huggins equation can be used to predict the phase diagram type and to estimate the liquidus curves. Literature data on dyes solubilities in LC of different classes are used for calculations.

The solubility parameters of components $\delta_i$ are calculated using the equation:

$$\delta_i = \left(\frac{\Delta v_{H_i} - RT}{V_i}\right)^{0.5},$$

where $\Delta v_{H_i}$, $V_i$ are the vaporization enthalpy and the molar volume of components at 298 K. The vaporization enthalpies of components are estimated basing on the group-contribution method (GCM). Data on density of mesogens are taken from [2] or calculated using the group-contribution methods.

The simple method based on the Hansen [3] solubility parameter estimation scheme was proposed. Solubility is correlated with the radius ($R_a$), which is calculated via the differences between the contributions of dispersion ($\delta_d$), polar interactions ($\delta_p$) and hydrogen bonding ($\delta_h$) of the solubility parameters [4].

$$R_a^2 = 4(\delta_d - \delta_{d2})^2 + (\delta_p - \delta_{p2})^2 + (\delta_h - \delta_{h2})^2.$$ 

The different scheme estimations for the solubility parameters and the thermodynamic properties are compared.

The knowledge on the intermolecular interactions in LC – dye systems gives a possibility to optimize a selection of dichroic dopant. Advantages and restrictions of GCM for the solubility curves estimation are discussed.

References:
A significant part of the energy in separation processes is typically converted to less useful forms or is lost, so thermodynamic analysis is a very effective tool in solving the problem of reducing energy consumption in the rectification process.

The aim of the work was to develop elements and software for the thermodynamic analysis of the rectification process. To achieve this aim, a number of tasks were solved.

In order to evaluate the efficiency of the separation process the thermodynamic analysis was carried out. In the course of the thermodynamic analysis the relationship of heat and work of a reversible process, the nature of occurrence and change of entropy of the system was determined. Also the expression for the calculation of the ideal and the real work of the separation was obtained. Moreover, the particular case of the calculation of the real work of separation with equal heat input to the cube of the column and withdrawn from the condenser was analyzed. On the basis of enthalpy diagrams we obtained the ratio of these heats, and their connection with the power state. In the case of the starting mixture having a temperature close to the boiling point, the two values of heat were equal.

The relationship of the thermodynamic criteria (the heat supplied to the cube of the columns, the work of separation and the production of entropy) was investigated, and it was shown that the optimum for each of the criteria was coincide with the draft version of the calculation of rectification. So the experiment confirmed theoretical results.

In the course of work the effect of heating of the starting mixture into the total costs was established. The starting mixture must be fed to the column at a reflux temperature. Heating should be carried out inside the apparatus. Elements of the thermodynamic analysis were presented in the form of software modules that allowed to calculate the ideal work of separation of the rectification process and to determine the efficiency of the process, as well as to calculate the criteria, which include the amount of time spent in the cube of the column, work of separation and entropy production.

The calculation of the number of freedom degrees for the column with the dividing wall and the column with the heat integration was carried out. The set of operating parameters of the process, that fixed the operation of the apparatus, was isolated. As an example, one could see the specification for each scheme.

In the Aspen Plus software package the work of separation of a binary mixture for the ideal process was calculated and its dependence on the composition of the starting mixture was obtained. Also the value of the ideal work per emission unit was calculated. Considering the thermodynamic analysis elements, the optimization of the actual rectification of the binary mixture of benzene and toluene was carried out. The optimization showed the best parameters of the column in terms of costs of the heat in the cube. According to the reports for the work of separation for the ideal and the real processes, the dependence of the efficiency of the fed mixture composition, which showed that the optimum situation is feeding a mixture of equimolar composition, was determined.
ESTIMATION OF LAMINAR-TURBULENT TRANSITION DETERMINATION, USING THE DEFINITION OF THE CURVES OF TURBULENT SPOT NUCLEATION AND GROWTH SPEEDS FROM THERMODYNAMIC FORCE


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The advantages of generalized calculation technique and investigation of formally analogous processes with the structural reconstruction of the original system are shown by means of estimation of laminar-turbulent transition dynamics, determining and using the curves of turbulent spot nucleation and growth speeds from thermodynamic force (the movement of relative kinetic energy ΔRe).

It was shown, that laminar-turbulent transition systems can be described, using the curves of turbulent «spot» nucleation and growth speeds, as a part of suggested generalized process analysis and calculation approach with structural reconstruction of the original system, relating to classical phase transition. Using the experimentally obtained estimations of conversion degree behavior in time \( \eta(\tau_e) \) (intermittency factor \( \gamma(\tau_e) \)) depending on the turbulent spots nucleation and growth curves, using Kolmogorov-Aavraami equation

\[
\eta(\tau_e) = \gamma(\tau_e) = \left[ 1 - \exp \left( -\frac{1}{3} \pi w_n v_g^3 (\frac{d^2}{v Re})^{n+1} \right) \right]
\]

where \( w_n \) – turbulent spot nucleation speed, \( v_g \) – turbulent spot linear growth speed, \( a \) – current distance from the beginning of the tube, \( d \) – diameter of the tube, \( \nu \) – water kinematic viscosity, \( Re \) – Reynolds number, the conversion degree, sizes, “turbulent spot” distribution function and related parameters were determined.

![Fig. 1. “Turbulent spot” nucleation speed as a function of Reynolds number.](image1.png)

![Fig. 2. “Turbulent spot” growth speed as a function of Reynolds number.](image2.png)

![Fig. 3. Conversion degree as a function of Reynolds number.](image3.png)
THE COMPUTING AND PHYSICAL EXPERIMENT FOR EVALUATING OF THE VARIABLE INTENSITY OF HEAT REMOVAL FROM THE SURFACE OF THE FALLING AND CRYSTALLIZING MELT DROPS DURING OF THEIR PRILLING

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The method of calculation of the intensity of heat removal from the surface of the crystallizing melt droplets are presented. A comparison with the experimental fixed values representing the intensity of the heat transfer between the surface of the resulting pellet and cooling agent are carried out.

The heat transfer coefficients on the surface of crystallizing pellet numerically were evaluated in depending upon the angle of attack of its by cooling agent flow $\varphi$ ($0, \pi$). The heat transfer coefficient $\alpha_c$ can be estimated by the following dependence:

$$\alpha_c = \frac{0.2 a_c}{Pr^\frac{n}{2} \sqrt{w/r_k \varphi}}, \quad (1)$$

where $Pr = \frac{v_c}{a_c} \alpha_c = \frac{r_k}{c p_c}$ – temperature conductivity coefficient, m$^2$/sec; $w$ – air velocity, m/sec; $r_k$ – pellet’s radius, m; $v_c$ – kinematic viscosity coefficient, m$^2$/sec; $c_c$ – heat capacity, J/kg·deg; $p_c$ – density, kg/m$^3$; $\varphi$ – the deviation of the angle of attack by cooling agent, degree. The calculated and experimental values of $\alpha_c$ and [1, 2] for pellets $1 \leq d \leq 3$ mm diameter at a hovering velocity $w_{hov}$ are shown in a Table. The average for the surface values of $\bar{\alpha}_c$ and the complete crystallization times $\tau_{mix}$ are tabulated.

<table>
<thead>
<tr>
<th>Estimation method</th>
<th>$\bar{\alpha}_c$, W/m$^2$·deg</th>
<th>$\bar{\alpha}_c^{calc}$, W/m$^2$·deg</th>
<th>$\bar{\alpha}_c/\alpha_c^{calc}$</th>
<th>Disarrangement, $\bar{\alpha}_c$ with $\alpha_c^{calc}$, %</th>
<th>$\tau_{mix}$, sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Experimental value [1] $d_k = 0.001$ m, $t_{mix} = 173$ºC</td>
<td>462,9</td>
<td>580,0</td>
<td>0,798</td>
<td>20,2</td>
<td>1,8</td>
</tr>
<tr>
<td>2. Frossling correlation computation [1] $d_k = 0.001$ m, $t_{mix} = 173$ºC</td>
<td>558,9</td>
<td>1304,1</td>
<td>0,429</td>
<td>57,1</td>
<td>2,0</td>
</tr>
<tr>
<td>3. Boundary-layer approximation computation $d_k = 0.001$ m, $t_{mix} = 173$ºC</td>
<td>108,8</td>
<td>168,8</td>
<td>0,645</td>
<td>35,5</td>
<td>2,0</td>
</tr>
</tbody>
</table>

The equation (1) for calculation $\alpha_c$ allows to estimate the variable intensity of heat removal on the surface of the pellet. Calculated and experimental [1, 2] data are corresponding. Averaged values $\bar{\alpha}_c$ also correlated with calculated values $\bar{\alpha}_c$. However, to consider the problem of calculating the $\alpha_c$ is solved prematurely.

References:
Biocompatibility, unique activity, structural and mechanical similarity of human bone tissue allows synthetic hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) to be widely used in modern medicine, and materials science [1]. This property is characteristic not only of hydroxyapatite, but of all the calcium phosphate phosphoric acid [2].

![X-ray diffraction chart](image)

Fig. 1. A comparative chart of X-ray of 6 samples.

Sample 1-1 obtained by the classical method of preparation, at temperature 60 °C ohmic heating and the introduction of phosphate solution dropwise in a solution of calcium nitrate. 1-2 obtained at temperature 60 °C ohmic heating, then their complete merging occurred at a constant temperature and correcting pH. 1-3 obtained at temperature 60 °C, under drip mixing, heating produced by microwave radiation. 1-4 received identical to sample 1-3, synthesis takes place at temperatures 100 °C, on the basis of thermodynamic conditions, as the Gibbs energy at 60 °C reaction is -1134 kJ, at 100 °C – -3381,31 kJ. 1-5 obtained under the conditions obtaining 1-4, after synthesis product was subjected to aging in the mother liquor for 24 hours. 1-6 obtained by synthesis condition 1-2, after synthesis of the precipitate was washed, and immediately headed to filter and smooth firing to 400 °C, with speed 1 °C/min. According to X–ray diffraction shown in Figure 1 in the crystalline phase sample application 1-1–1-6 corresponds to hydroxyapatite. Most crystallized sample is obtained under the designation 1–6. The reaction product is hydroxyapatite and $\beta$–TCP (< 20 %).

Thus, it is shown that the synthesis of 6 is most optimal to obtain a single–phase powder with minimal time and labor costs. Since the samples 1,2,3,4 and 5 showed no apparent efficacy, further examples will not be considered, however, sample number 1 is considered as a control.

Conclusions:
1. Various methods of synthesis of hydroxyapatite were investigated, conducted a comparative analysis, based on the assumptions that had arisen in the course of the synthesis the own synthesis was developed using known techniques.
2. The results show that the method of heating does not affect the state of the final product. Preferably conduct complete merging reagents at a temperature close to the boiling point as a reactant introduction drip apparently showed no effect.

References:
SELECTION OF EXTRACTIVE AGENTS FOR SEPARATING ACETONE – CHLOROFORM – METHANOL MIXTURE

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Extractive distillation (ED) is the primary method for separating mixtures in technologies of basic organic and petrochemical synthesis. Choice of selective agents providing energy decrease of ED-complexes is a priority task in the design of separation flowsheets.

For ED of binary azeotropic mixtures was suggested to choose the extractive agent on the largest maximum difference between the values of the excess Gibbs energy of binary mixtures formed by the components of the basic mixture (1, 2) and the selective separating agent (SA): \( \Delta(\Delta g^E) = \Delta g^E_{1-E} - \Delta g^E_{2-E} \). Agent is selective if \( \Delta(\Delta g^E) \) values exceeds 1000 J/mol. This approach was applied to the choice of agents for the separation of ternary mixtures showing only positive deviation from ideal behavior [1]. The condition \( \Delta(\Delta g^E) \geq 1000 \text{ J/mol} \) to be respected for each binary azeotropic system:

\[
\Delta(\Delta g^E) = \Delta g^E_{1-E} - \Delta g^E_{2-E}, \quad \Delta(\Delta g^E) = \Delta g^E_{1-E} - \Delta g^E_{3-E}; \quad \Delta(\Delta g^E) = \Delta g^E_{2-E} - \Delta g^E_{3-E}.
\]

Here agents selection procedure for the ED acetone (A) - chloroform (C) - methanol (M) is realized. There are ternary saddle azeotrope, two positive azeotropes (A - M, C - M) and negative azeotrope A - C. Selection of single agent for the separation of ternary mixtures with opposite deviations from ideal behavior in binary systems is more difficult. SA should form the intermolecular interactions of different chemical nature with original components. Besides all solvents must satisfy the common requirements to extractive agent, first of all selectively increase the volatility of substances to be separated, do not form azeotropes with them.

High-boiling solvents namely dimethyl sulfoxide (DMSO), ethylene glycol (EG), monoethanolamine (MEA) correspond these requirements. At the same thermodynamic criterion \( \Delta(\Delta g^E) \geq 1000 \text{ J/mol} \) for MEA is satisfied only for binary mixtures containing methanol. DMSO and EG are not selective for methanol - chloroform: \( \Delta(\Delta g^E) \) not exceeds 150 J/mol. No single agent, selective with respect to all binary mixtures. Thus, use of two different agents is required.

Simultaneous input of any two SA in column 1 did not solve the problem of A-C-M separation. It is necessary to introduce the agents in different columns taking into account the criteria \( \Delta(\Delta g^E) \). Valid flowsheet consist of two ED-complexes: 1) column 1 - ED original mixture with MEA for isolation mixture A-C (distillate product), column 2 - distillation M - MEA; 2) column 3 - ED mixture A-C with EG, column 4 - separation C from EG. ED-flowsheet was calculated for 100 kmol/h equimolar mixture A-C-M at 101.32 kPa. Flow ratios F:F_{SA} are 1:1 (column 1, SA - MEA) and 1.5:1 (column 3, SA - EG). Energy consumption of ED-complexes is about 2398 and 2127 kJ. It was obtained the commercial quality of all components.

Reference:
In this paper presents the results of kinetic studies hydrogenation of 1,5-cis,cis-cyclooctadiene and dicyclopentadiene (endo-tricyclo[5.2.1.0²,⁶]decadiene-3,8), to assess the relative reactivity of the double bonds, and the sequences of their saturation.

It was established that velocity of the saturation of the first double bond in the cyclooctadiene by hydrogen in the liquid phase with using the finely divided catalyst (1% Pd / C) higher than the velocity of hydrogenation second double bond (W₁ / W₂ = 10 ÷ 11) at hydrogenation in the absence of a solvent or in solution. Thus, the rate of hydrogenation of 1,5-cis,cis-cyclooctadiene to cyclooctene in 10 times higher than the rate of hydrogenation of the cis-cyclooctene to cyclooctane, despite the fact that the double bonds of C₈ cycle are rehybridized the equally.

To explain this difference, we taken into account the fact that the reactivity of the double bond in saturation process using a heterogeneous catalyst is correlated with the electron-donating properties. This property of the double bond yields efficacy at molecules chemisorption on the catalyst surface.

It is shown that reactivity of the cyclooctadiene is abnormally high since diene has the conjugated system of double bonds as a result of the implementation of a consistent positional isomerisation of double bonds on the surface of the catalyst.

The double bonds of the dicyclopentadiene molecule are isolated and the double bond of bicycloheptene moiety saturating as the first in according to the results of spectroscopy (¹H NMR and COSY). The velocity of saturation at the hydrogenation of dicyclopentadiene to dicyclopentene higher than the same value at the hydrogenation of the cyclooctadiene to cyclooctene. Consequently, the electron-donor properties of the double bond bicycloheptene moiety of dicyclopentadiene molecule exceed similar properties of the conjugated system double bonds of cyclooctadiene.

At the same time, the double bond of cyclooctene in process its hydrogenation in cyclooctane saturates at a higher speed, compared with the double bond of the C₅ cycle of dicyclopentene – the cycle normal size.

Differentiation in speeds in the hydrogenation of double bonds of dicyclopentadiene (W₁ / W₂ = 7 ÷ 9) is due, above all, by the use of aromatic solvents (toluene). This difference in speeds hydrogenation of the first and second the double bond of cycloienes (1,5-cyclooctadiene and dicyclopentadiene) enables selectively obtain the corresponding cycloalkenes (dicyclopenten and cyclooctene) in the process their hydrogenation.

It was shown that the kinetics of the hydrogenation of cyclic dienes in the implementation of the process in a flow reactor of perfect mixing is modeled in accordance with the Langmuir-Hinshelwood equation.
For the apparatuses with mixers the nominal drive power $N_{dr}$ is estimated on magnitude of the operating power $N_{op}$ in view of the start-up period $T_{st}$: 
\[ N_{dr} \geq k_{st} N_{op} / \eta, \quad T_{st} \leq 12 \text{ sec}, \]
where $k_{st} = 1...4$ – is the correction factor; $\eta < 1$ – is the drive efficiency.

The regularity $N(\tau)$ of the power reduction from $N_{st} = N(\tau = 0)$ to $N_{op} = N(\tau = T_{st})$ and, hence, the amendment $k_{st}$ can not be calculated analytically precisely. Therefore, we have proposed the “strong-willed” model two-parameter [1]
\[
N_{\chi} = 1 + \varepsilon_{st} \left[ 1 - \left( \frac{2\varepsilon}{1 + \varepsilon} \right)^{\chi} \right], \quad \text{(1)}
\]
where $N_{\chi}(\tau \leq T_{st}) = N / N_{op} \geq 1$ – is the instantaneous power in the operating units of P; $\varepsilon_{st} = N_{st} - 1 > 0$ – is the relative values of the difference $N_{st}$ and $N_{op}$; $N_{\chi} = N_{st} / N_{op} > 1$ – is the dimensionless starting power; $\varepsilon = \tau / T_{st} \leq 1$ – is the time in the units of $T_{st}$.

Parameter $\chi > 0$ sets the character of the power change and, in particular, defines the energy consumption ($\bar{W}_{st} = W_{st} / W_{op}$) on acceleration of the liquid medium in start-up period
\[
\varepsilon_{W} = \bar{W}_{st} - 1 = \int_{0}^{\frac{2\varepsilon}{1 + \varepsilon}} \frac{1}{\varepsilon_{st}} d\varepsilon_{st} = \left[ 1 - \frac{2\varepsilon}{1 + \varepsilon} \right] \varepsilon_{st}, \quad \text{(2)}
\]
where in the dimensional magnitudes $W_{op} = N_{op} T_{st}$ ($\bar{W}_{op} = 1$) – is the energy (J) for “ideal” (inertia resistance $\square 0$) conditions at starting of the drive: $W_{st} = W_{op} \Leftrightarrow \varepsilon_{W}^{id} = 0$. It is obvious that in the framework of the inequality $T_{st} \leq 12$ sec on magnitude $\varepsilon_{W}$ of the relative difference $W_{st}$ and $W_{op}$ we can judge about the value of the correction factor $k_{st}(\varepsilon_{W})$.

The dependence of $\varepsilon_{W}(\chi)$ (2) for different values of $\varepsilon_{st}$: $1 - \varepsilon_{st} = 1$; $2 - 2$; $3 - \varepsilon_{st} = 3$.

Selecting a specific values of the parameters $\chi$ and $\varepsilon_{st}$ is determined by the acceptable accuracy of approximation of the experimental curve $N_{\chi}^{exp}(\varepsilon)$ by the calculation model (1)
\[
N_{\chi}^{exp}(\varepsilon) \approx N_{cal}(\varepsilon) \Rightarrow \chi, \quad \varepsilon_{st} \Rightarrow \varepsilon_{W} \Rightarrow k_{st}. \quad \text{(3)}
\]

Reference:
ESTIMATION OF ENERGY CONSUMPTION ON SEPARATION OF MIXTURES IN COMPLEXES BASED ON A COMBINATION OF RECTIFICATION AND SPLITTING PROCESSES

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The flowsheet of the separation of mixtures of different nature Butanol (1) – Water (2) – Toluene (3) and Isopropyl alcohol (1) – Acetonitrile (2) – Hexane (3) is considered (Figure 1). The structure of the phase diagrams is given in Figure 2. It is necessary to define two variables to calculate material balance: composition of streams $R_{1f}$ and $B$. According to the separation condition composition of stream $B$ belongs to the separatrix $S_2$. Composition of stream $R_{1f}$ coincides with ternary azeotrope (I) or belongs to separatrices $S_1(II), S_2(III)$ for the system (a) and $R_{1f}$ coincides belongs to separatrices $S_1(I, III), S_2(II, IV)$ for the system (b).

![Fig. 1. Flowsheet of separation of ternary mixtures.](image)

![Fig. 2. Phase diagram of systems: a) Butanol (1) – Water (2) – Toluene (3) and b) Isopropyl alcohol (1) – Acetonitrile (2) – Hexane (3).](image)

The influence of the composition $R_{1f}$ and amount of recycle streams (A and B) on energy consumption (Table) for the feed composition ($x_1 = 0.8; x_2 = 0.1; x_3 = 0.1$ w.p.) was studied.

<table>
<thead>
<tr>
<th>System</th>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location of $R_{1f}$</td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>$\Sigma R$, kmol/h</td>
<td>0.47</td>
<td>1.27</td>
</tr>
<tr>
<td>Energy consumption, kW</td>
<td>24.4</td>
<td>194.4</td>
</tr>
</tbody>
</table>

As can be seen, energetically favorable is mode in which composition of $R_{1f}$ coincides with ternary azeotrope (Ia) or is located near separatrix $S_2$ (IVb).
THE MECHANISM OF LOW-TEMPERATURE CARBON MONOXIDE OXIDATION BY MOLECULAR OXYGEN ON PdCl$_2$-CuCl$_2$/\(\gamma\)-Al$_2$O$_3$ CATALYST


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The low-temperature (15–100°C) oxidation of carbon monoxide by oxygen is of fundamental scientific interest because it is one of the simplest oxidation reactions and can be used to establish general laws governing oxidation processes.

Among the low-temperature catalysts for this reaction, supported metal complex catalysts are least studied. Palladium-copper-based catalysts are the most promising of this group [1-3]. This report deals with new data about kinetics and mechanism of low-temperature carbon monoxide oxidation by molecular oxygen on PdCl$_2$-CuCl$_2$/\(\gamma\)-Al$_2$O$_3$ catalyst.

Previously, the state of the active constituents of the freshly prepared PdCl$_2$–CuCl$_2$/\(\gamma\)-Al$_2$O$_3$ catalyst for the low-temperature oxidation of the carbon monoxide by molecular oxygen was studied by X-ray absorption spectroscopy (XAS), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) and preliminary kinetic investigation was carried out [3,4].

The kinetic regularities were studied under atmospheric pressure gas mixture of CO, N$_2$, O$_2$ and H$_2$O in a glass thermostated flow reactor at steady-state conditions when conversion of the reactants is less than 15 % (differential reactor). A systematic study of the reaction kinetics was studied by the method of single-factor experiment with a wide variation range of oxygen, water, and carbon monoxide partial pressures. The study of mechanism was performed using the procedures of the advancing hypotheses about the mechanism on the basis of known physico-chemical data [4] and model of Langmuir – Hinshelwood, and discrimination of ones using kinetic data. Adequate structural kinetic model of the low-temperature oxidation of carbon monoxide is developed. It has been shown that the most probable mechanism of the reaction under consideration includes carbon dioxide formation by interacting the surface complexes of Pd(I) and Pd(II), coordinating carbon monoxide and water, with surface complexes Cu(I), coordinating molecular oxygen.

Acknowledgements

This work was supported by Russian Foundation for Basic Research (grant No. 16-33-00482).

References:
Gas chromatography (GC) is, besides a powerful tool for the analysis of complex mixtures, an alternative to the calorimetric and static methods for measuring physicochemical parameters of solutes [1]. In our previous works [2-4] we presented enthalpies of sorption \( \Delta s_sC_{(298,2K)} \) measured by GC on capillary column with non-polar stationary liquid phase (OV-101, BP 1) and vaporization enthalpies \( \Delta_{vap}H^o(298,2K) \) calculated from temperature dependences of experimental values of vapor pressures for pure oxygen-containing compounds: monoalkyl ethers of mono and polyethylene glycols, acetalts and alkyl ethers of glycerol. In the present work, the excess enthalpy \( \Delta C_E^\infty(T) \) was calculated based on values of \( \Delta s_sC_{(298,2K)} \) и \( \Delta_{vap}H^o(298,2K) \):

\[
\Delta C_E^\infty(T) = \Delta_{vap}H^o(T) + \Delta s_sC_{(298,2K)}
\]

(1)

In order to compare, the meaning of \( \Delta C_E^\infty(T) \) was also calculated from the equation (2), based on temperature dependence of activity coefficient \( \gamma^\infty \):

\[
\ln(\gamma^\infty) = \frac{\Delta C_E^\infty(T)}{R} = \frac{\Delta s_sC_{(298,2K)}}{R}
\]

(2)

Values obtained by both methods were near to each other. As the result of our calculation, all investigated substances were divided into 3 groups: 1 – substances with one hydroxyl-group in the structure of molecules, 2 – substances with two hydroxyl-groups, 3 – substances without hydroxyl-groups. The value of \( \Delta C_E^\infty(298K) \) change slightly within each group. Therefore, the average value of \( \Delta C_E^\infty(298K) \) was calculated for each group (See fig. 1).

Substances with one hydroxyl-group (1 group)
- polyethylene glycols
  - R = t-C4; n=1-3
- 1,3-diethoxypropanol-2
  - \( \Delta H^{E,\infty}(298,2K)_{av} = 7,3 \text{ kJ/mol} \)

Substances with two hydroxyl-groups (2 group)
- monoalkyl ethers of glycerol
  - R = C1, C2, t-C4
  - \( \Delta H^{E,\infty}(298,2K)_{av} = 19,9 \text{ kJ/mol} \)

Substances without hydroxyl-groups (3 group)
- alkylaldehyde diethyl acetal
  - R = C2, C3, i-C3
- alcoxyacetaldehyde diethyl acetal
  - R = CH2OCH3, CH2OC2H5
  - \( \Delta H^{E,\infty}(298,2K)_{av} = -4,2 \text{ kJ/mol} \)

Fig. 1. Average values of the excess enthalpy \( \Delta H^{E,\infty}(298,2K)_{av} \)

As we can see from the figure 1, values of \( \Delta H^{E,\infty}(298,2K)_{av} \) vary with the change of molecules’ structure. It means that the energy of intermolecular interaction at the liquid-gas transition depends on numbers of OH-groups in the molecules. The negative value of \( \Delta H^{E,\infty}(298K) \) of acetals shows stronger interaction between substances and siloxy-groups of liquid stationary phase than interaction between molecules of pure substances. Obtained values of \( \Delta H^{E,\infty}(298,2K)_{av} \) can be applied for prediction of \( \Delta_{vap}H^o(298,2K) \) of substances considered structures by eq. 3 upon condition a known value of \( \Delta s_sC_{(298,2K)} \):

\[
\Delta_{vap}H^o(298,2K) = -\Delta s_sC_{(298,2K)} + \Delta H^{E,\infty}(298,2K)_{av}
\]

(3)

Due to the content in wastewater of biologically resistant to oxidation organic compounds
technologies of water purification which underlaid use of strong oxidizers is are perspective.
Recently more and more authors give preference to methods which underlaid reactions of
generation of oxidizing agents. Electrochemical advanced oxidation processes are in such
technologies. Processes of electrochemical generation of hydroxyl radicals are the underlaid of a
method. It should be noted that can realize electrochemical technologies of produce hydroxyl
radicals both direct (anode oxidation), and indirect (cathodic remediation) methods.
Electrochemical generation of hydroxyl radicals and their role in electrochemical reactions of
transfer of oxygen depends on type of reaction, the mechanism and material of the used
electrode, and also character of the environment. The mechanism of formation of hydroxyl
radicals depends on electrode potential. In this regard the purpose of work consists in detailed
consideration of possible processes of obtain strong oxidizing agents.

At anode oxidation oxidizing agents (·OH) are formed on the anode in one stage through
water oxidation reaction:

\[ \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ + e^- \]

or through water decomposition reaction:

\[ (\text{H}_2\text{O})_{\text{ads}} \rightarrow (\text{H}^\cdot)_\text{ads} + (\text{HO}^\cdot)_\text{ads} \]

Materials of electrodes in these cases are Pt, PbO\textsubscript{2}, Ti, Ti/IrO\textsubscript{2}, Ti/RuO\textsubscript{2}, Ti/SnO\textsubscript{2}, Ti/Pt-Ir, Ti/PbO\textsubscript{2}, Ti/PdO-Co\textsubscript{3}O\textsubscript{4}, Ti/RhO\textsubscript{2}-TiO\textsubscript{2}, Ti/TiO\textsubscript{2}-RuO\textsubscript{2}-IrO\textsubscript{2}, Ti/SnO\textsubscript{2}-RuO\textsubscript{2}-IrO\textsubscript{2}, Ti/SnO\textsubscript{2}-Sn, Ti/RuO\textsubscript{2} electrodes and a diamond electrode, doped boron. It is established that Ti/Pt-Ir and
Ti/PdO-Co\textsubscript{3}O\textsubscript{4} anodes provide the high speed of removal of organic substances. In technology of
water purification practical development and industrial application have received the titanic
anodes covered with an active layer from the mixed isomorphic TiO\textsubscript{2} and RuO\textsubscript{2} oxides, so-called
oxide-ruthenic titanic anodes.

In case of the indirect method of a ·OH particle receive Fenton’s reaction through
remediation of O\textsubscript{2} on the cathode to H\textsubscript{2}O\textsubscript{2}, and to enter Fe\textsuperscript{2+} ions into solution, or generate
electrochemical in the way:

\[ \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \]
\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \]
\[ \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}^+ + e^- \]
\[ \text{HO}_2^- \rightarrow \text{O}_2 + \text{H}^+ + e^- \]

As electrode materials in this case serve graphite, gas-diffusive carbon, steel, mesh glass
carbon, felt carbon, O\textsubscript{2} - diffusive electrodes, platinum.

In case of use of a gas-diffusive electrode on the cathode reaction of two-electronic
remediation of oxygen to hydroperoxide ion proceeds:

\[ \text{O}_2 + 2e^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{OH}^- \]

On the anode reaction of oxidation of water with formation as HO intermediate· - radicals
proceeds:

\[ 2\text{H}_2\text{O} \rightarrow 2\text{HO}_2^- + 2\text{H}^+ + 2e^- \]
Comparative Assessment of Chemical, Electrochemical, Photochemical and Photocatalytic Processes of Treatment of the Wastewater Containing the Resistant to Oxidation Organic Compounds

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Today oxidizing processing of wastewater is the most demanded (popular). The possibility of more effective implementation of process of water purification, and also use of nontoxic oxidizers is the reason. According to literary data, distinguish chemical, electrochemical, photochemical and photocatalytic oxidizing systems. Carry to chemical systems: H$_2$O$_2$/Fe$^{2+}$, O$_3$/Fe$^{2+}$, O$_3$/Cu$^{2+}$, H$_2$O$_2$/Cu$^{2+}$, carry to electrochemical systems: H$_2$O$_2$/Fe$^{2+}$, carry to photochemical systems: H$_2$O$_2$/UV, O$_3$/UV, H$_2$O$_2$/ O$_3$/UV, carry to photocatalytic systems: O$_3$/Fe$^{2+}$/UV, H$_2$O$_2$/Fe$^{2+}$/UV, O$_3$/Fe$^{2+}$/UV /Cu$^{2+}$.

The purpose of work is the comparative analysis of oxidizing force of various systems and their ability to influence effectively the hardly oxidized organic components of wastewater. Comparison of systems: H$_2$O$_2$/Fe$^{2+}$ - a chemical way, H$_2$O$_2$/Fe$^{2+}$ - electrochemical and H$_2$O$_2$/Fe$^{2+}$/UV shows that the photocatalytic system has advantage. First, the oxidant – H$_2$O$_2$ can be generated two-electronic transformation of oxygen on the cathode. As material of the cathode serves mesh glass carbon, felt carbon, O$_2$ - diffusive electrodes.

O$_2$ + 2H$^+$ + 2e$^-$ → H$_2$O$_2$

In this case the polluting substances can be oxidized not only the electrogenerated hydrogen peroxide molecules, but also ·OH particles created on the anode:

Fe$^{2+}$ + HO· → Fe$^{3+}$ + OH$^-$

Increase in oxidizing force of the electrolytic H$_2$O$_2$/Fe$^{2+}$ system is connected with addition of small quantities of Fe$^{2+}$ (catalyst) which react with hydrogen peroxide before formation of ·OH of particles:

Fe$^{2+}$ + H$_2$O$_2$ → Fe$^{3+}$ + OH$^-$ + HO·

In these conditions the hardly oxidized organic substances destruction, mainly, the combined attack on the anode and in the environment.

Process of generation of radicals can be also carried out in the chemical way:

Fe$^{2+}$ + H$_2$O$_2$ → Fe$^{3+}$ + OH$^-$ + HO·

However a lack of the last way is need of optimization of ratios [H$_2$O$_2$]/[Fe$^{2+}$] and [Fe$^{2+}$][RH]. At this pH also is important the parameter as his magnitude promotes interaction of organic substance with reagent in the maximum degree. Processes of UV-oxidation include generation of radicals through UV-photolysis of hydrogen peroxide. Interaction of peroxide of hydrogen and quanta of UV-irradiation leads to formation of ·OH of particles due to homolytical splitting (breakage) of peroxide of hydrogen:

H$_2$O$_2$ + hv → 2HO·
Activity coefficients at infinite dilution are used for the choice of entrainers for extractive distillation of binary mixtures. Generally considered the separation of azeotropic mixtures.

There are the results choice selective agents for the extractive distillation of zeotropic mixture methanol - ethanol and acetone - water. The alcohols mixtures are characterized by the values of relative volatility close to unity, the tangential azeotrope is present in the system acetone - water at atmospheric pressure.

High-boiling solvents tested as entrainers are N-methylpyrrolidone (NMP), cyclohexanol (Col), cyclohexanone (Con), dimethyl sulfoxide (DMSO) and diols: ethylene glycol (EG), 1,3-propanediol (PD), 1,4-butanediol (BD). The new data for methanol and ethanol activity coefficients at infinite dilution of entrainers were obtained by gas-liquid chromatography (GLC).

The experiments were performed using a Chromos 1000 gas chromatograph equipped with a thermal conductivity detector. The column preparation and the packing method used in this work have been described previously, experimental technique has been tested too [1]. Glass columns of length 1 m and 3 mm internal diameter were used. Chromosorb P 60/80 mesh supplied by Johns Nahville Products was used as the solid support.

Entrainer's selectivities $S_{\infty}$ were calculated from the corrected retention times of substances ($t_{R_i}$, sec) as $S_{\infty} = \frac{t_{R_1}}{t_{R_2}}$.

It is found that the selectivity $S_{\infty}$ for methanol - ethanol system changes as follows: DMSO - 1.116, EG - 1.155, PD - 1.342, BD - 1.425, NMP - 1.543, Con - 1.585, Col - 1.822. When extractive distillation is projected to receive methanol in the distillate. These values were compared with those of mixed entrainers EG - DMSO and NMP - DMSO. Experiments were carried out for different compositions of mixed solvents: 25, 50 and 75 wt. % DMSO. The maximum selectivity for mixed agents are observed at 50 wt. %: 1.196 for EG - DMSO and 1.705 for NMP - DMSO. Thus, mixed agents exhibit higher selectivity in comparison with the individual solvents.

For separate a mixture of acetone - water may be used any agent. It is projected to receive acetone in the distillate of the extractive distillation column. All solvents exhibit significant selective properties. For example, the smallest value $S_{\infty}$ is 9.862 for NMP.

Acknowledgements
This study was financially supported by the Ministry of Education and Science of the Russian Federation (grant No. 2014/114, project 2065).

Reference:
Section 2

Advanced Processing at Petrochemistry and Organic Synthesis
BENZENE–CYCLOHEXANE–TOLUENE MIXTURE EXTRACTIVE DISTILLATION IN THERMALLY COUPLED COLUMNS

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Benzene is one of the important raw materials for organic synthesis. World production of benzene now exceeds 50 million tons per year. Therefore, the reduction of energy consumption in this process is an actual task. Extraction and extractive distillation (ED) are used for the recovering of benzene from petroleum and coking coal products. ED is occurred by introducing an additional component, the so-called entrainer, as an independent additional feed into the column to facilitate a separation.

Recently, the systems with partially thermally coupled distillation columns (PTCDC) have been applied to reduce the energy consumption of ED. Anokhina et al [1] considered the ED with N-methylpyrrolidone (NMP) as the entrainer of benzene (B), cyclohexane (CH) and toluene (T) mixture as some equivalent of the crude benzene fraction. Three conventional ED schemes consisting of three columns with two outlets and seven ED schemes with PTCDC were investigated. All 10 schemes were compared by the total reboiler heat duties. The flowsheets were simulated for the initial mixture contained 78, 12, 10 mass % of B, CH, T respectively. It was found, that PTCDCs decreased the energy consumption in the column boilers up to 28.7 % compared to the conventional ED flowsheets.

The aim of this work is to identify ED flowsheet with the lowest energy consumption for two different other initial feed compositions: mixture 1 – the product of catalytic dealkylation of the gasoline fraction of hydrocracking with 40, 20, 40 mass % of B, CH, T respectively, and mixture 2 – the product of vapor cracking gasoline hydrocracking and hydropurification with 50, 5, 45 mass % of B, CH, T respectively. Three conventional ED schemes and five ED schemes consisting of one simple column and PTCDC with side section have been considered. All 8 schemes have been compared by the total reboiler heat duties ($Q_\Sigma$). $Q_\Sigma$ value was determined for each scheme under optimal values of operating parameters.

The flowsheets were simulated under the next conditions: the initial mixture flow rate was 15000 kg/h; the purities of products were assigned to B and CH as 99.9 mass %, for T as 99.75 mass %; the entrainer flow rate contained 99.99 mass % NMP; the entrainer temperature was fixed as 70 °C; the operating pressure was equal 101.3 kPa. NRTL model was used to predict the activity coefficients. For three conventional schemes optimization variables include the entrainer flow rate, the entrainer and the feed trays locations. For the schemes with PTCDS the optimization variables include the side outlet tray location and the value of flow rate directed to side section. Optimization was carried out by using sensitivity analysis and the SQP (sequential quadratic programming) optimization tool from Aspen Plus.

It has been determined that for two initial feed compositions the scheme where toluene is separated in the first column as the bottom product has the lowest energy consumption among the three conventional schemes. The best solution with PTCDC in the both cases is a scheme where at the first ED column CH is recovered as a distillate and B and T are distillates of the main column and side section of complex column, respectively. This power consumptions decrease by 20-22% in comparison with conventional ED schemes with two outlets columns.

Reference:
Bitumen and heavy oil are close on the physical and chemical properties to the heavy remains of atmospheric distillation usual petroleum. For this purpose, they can serve as initial raw materials for usual installations of oil refineries. However, such approach to a problem considerable would narrow the wide range of the received products and their commodity characteristics. Therefore, bitumen and heavy oil should consider as complex raw materials which allow to receive a wide set of finished commodity products.

Bitumen are a perspective source of hydrocarbon raw materials as in Kazakhstan about 150 fields with the maintenance of organic parts from 5 to 45% and above depending on depth of their bedding are concentrated. In this regard there is an urgent need to strengthen researches on deep studying of physical and chemical characteristics of bitumen and heavy oil to receiving from them valuable hydrocarbon raw materials which find broad application in chemical and petroleum industry.

In work as object of research considered the most large-scale and perspective deposit of Karasyaz-Taspas bitumen field of Mangyshlak which reserve over 33 million ton.

Results of laboratory studies show that the content of organic substances in bitumen of the Karasyaz-Taspas field changes over a wide range from 1,15 to 20,06% (the average content of 9,66%), belongs to the class malt: viscous, pitch substances of black colour. Density changes within 0,9224 ÷ 0,9731 g/cm³, the average content of sulphur – 0,19%.

Maintenance of high-viscosity components (group chemical composition): asphalting of 10,86 ÷ 20,54%, oils 53 ÷ 64% and pitch 24 ÷ 31% mass of organic part.

By results of laboratory researches at an atmospheric distillation received synthetic petroleum Karasyaz-Taspas fields it is possible to receive the whole set of hydrocarbon components. Natural bitumen from bitumen are united by easy fractions, boiling away to 200°C, and in synthetic petroleum, depending on processing process, an exit of petrol fractions can make 10 – 20%.

Also data on researches of group hydrocarbon structure, physical and chemical characteristics petrol fractions are provided in work.

When processing bitumen also the content of impurity of vanadium and nickel are important. Presence of these metals negatively influences activity and selectivity of catalysts of process of catalytic cracking petrol fractions which purpose is increase of octane number.

Full extraction of valuable metals from mineral bitumen are one of the perspective directions of the near future which gives the chance to optimize the existing schemes of oil processing with a possibility of receiving in addition metal-containing products.

Follows from the above that the received synthetic oil from bitumen surpasses the characteristic in characteristics usual petroleum, and at her processing according to the usual technological scheme it is possible to receive the whole set of hydrocarbon components.

Thus, follows from the above that on individual group structure petrol fractions from synthetic petroleum from bitumen can be applied as automobile fuels or as raw materials to pyrolysis with receiving olefin hydrocarbons for chemical industry.
LIQUID-PHASE SYNTHESIS OF CYCLOHEXYLMINE USING VIII-GROUP METALS STABILIZED IN HYPERCROSSLINKED POLYSTYRENE

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Cyclohexylamine and its derivatives are widely used in modern industry as intermediates in the synthesis of caprolactam, N-cyclohexyl-2-benzothiazole sulfenamide (accelerator of vulcanization process and inhibitor of metal corrosion). Moreover, cyclohexylamine and its derivatives are used in the synthesis of pharmaceutical substances and insecticides [1]. In modern industry, both gas-phase and liquid-phase syntheses of cyclohexylamine by the reduction of aniline or nitrotoluene with hydrogen using heterogeneous catalysts are implemented [1–3]. In all the cases, significant amounts of by-products, i.e. dicyclohexylamine and ammonia, are formed. In some cases the formation of diphenylamine, N-phenylcyclohexylamine, cyclohexane and benzene at elevated temperatures also observed [4]. As follows from literature, the selectivity of the process of liquid-phase reduction of aniline can vary noticeably depending on the catalyst nature. Best results (selectivity of 95% with respect to cyclohexylamine) are achieved while using ruthenium catalysts supported on inorganic supports [4]. It is noteworthy that the increase of reaction duration while using ruthenium catalysts allows obtaining dicyclohexylamine with the selectivity up to 99.9% [5], and 99% of selectivity while using cobalt catalysts [6, 7].

This research is directed to the study of the process of liquid-phase synthesis of cyclohexylamine using ruthenium-, platinum- and palladium-containing catalysts based on metal nanoparticles stabilized in polymer networks of hypercrosslinked polystyrene. All the catalytic systems were reduced in hydrogen flow at 300°C before the testing. During the catalytic testing the nature of the solvent, temperature, concentration of aniline and hydrogen pressure were varied. The catalyze content was studied by gas chromatography-mass spectrometry. The stability of synthesized catalytic systems as well as transformation of active metals on catalyst surface were studied by infrared diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, low-temperature nitrogen physisorption, and thermogravimetry. It was shown that the synthesized metal-containing systems remain stable during multiple repeated uses.

Acknowledgments
This work was funded by the Russian Foundation for Basic Research (grant 16-08-00355).

References:
A CONVENIENT SYNTHESIS OF Li-SILANOLATES BY NON-EQUILIBRIUM ION EXCHANGE PROCESS

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Alkali metal organosilanolates are active agents for cleavage of Si-O bonds. They are widely used as initiators of anionic ring opening polymerization (ROP) of cyclosiloxanes and catalytic rearrangement of linear and cyclic oligosiloxanes [1,2], as nucleophilic reagents for substitution reactions, as well as intermediates in the synthesis of random and block copolymers of different molecular architecture [3]. The most important application Li-silanlates found in anionic ROP of cyclosiloxanes for the synthesis of macromolecules with a narrow MWD.

The reduced reactivity of Li-silanlates limits contribution of side redistribution reactions of siloxane units in the synthesis of macromolecules with complex molecular architecture [2]. And finally, an attractive feature Li-silanlates in contrary of Na and K derivatives is a higher solubility in organic media.

Unfortunately, customary synthesis of Li-silanlates [4] through Li-organic reagents are complicated and require special equipment.

In this work we propose a simple and convenient synthesis Li-organosilanolates on the basis of available raw materials – Na- and K-organosilanolates by ionic exchange reactions with LiCl.

For this purpose we studied the interaction of LiCl with various alkali salts of silanoles, for example:

- Sodium trimetilsilanolate Me₃SiONa;
- Na- salts of α, ω-(dihydroxy)-oligodimethylsiloxanes NaO (Me₂SiO)₂₃Na;
- organosilanolates of general formula [RSiOOM]₃⁻⁴ (R = Ph, Vin; M = Na (K);
- organo(ehoxy)slanolates of general formula RSi(OEt)₃ONa (R = Ph, Me, Vin)

In general terms, the process described by the scheme:

\[
\begin{align*}
\text{Si} &\text{O} &\text{M} &\text{LiCl} \\
\text{MCl} &\rightarrow &\text{Si} &\text{O} &\text{Li}
\end{align*}
\]

Reactions were carried out under mild "non-equilibrium" conditions in absolute ethanol (THF). The resulting NaCl (KCl) drops out as a precipitate.

As a result, produced Li-organosilanolates (yields ≥85%), in which degree of substitution of Na⁺ (K⁺) ions to Li⁺ reaches 90%.

References:

LIQUID-PHASE HYDROGENATION OF AROMATIC RING IN FUELS USING METALS OF VIII-GROUP STABILIZED IN HYPERCROSSLINKED POLYSTYRENE

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The hydrogenation of benzene to cyclohexane is used to probe the activity of catalysts for reactions taking place on metal sites. Moreover, this reaction is of practical interest as special attention has recently been focused on the hydrogenation of aromatic compounds and there is an increasing demand for suppression of the benzene content in petroleum fuels and especially in gasoline and diesel in the near future. The support used to disperse a metal has a significant effect on the catalyst activity for hydrogenation of benzene. Various forms of interaction between active metal and support materials in supported metal catalysts have been cited in the literature to explain experimental observations. In cases where metal aggregates are smaller than 1 nm and nearly molecular in character, interaction with the support can be stronger and more complex. It has been observed that the activity of very small metal clusters may be lower in comparison to larger clusters. Therefore, for the hydrogenation of benzene, which is frequently regarded as a structure insensitive reaction on supported metals sites, there are some divergences, particularly in the case of small metal particles. Moreover, data indicating divergences from structure insensitivity have appeared in several studies particularly on nickel catalysts, but also on other metals deposited on various supports. Modern catalysts of hydrogenation of aromatic compounds are based on inorganic supports. In these systems, metal is located on the surface and can be easily washed out by the abrasion during the catalytic cycle, which reduces the catalyst life-time. Metal-containing systems stabilized in hypercrosslinked polymers can overcome this disadvantage.

This research is directed to the study of the process of liquid-phase benzene hydrogenation in alkanes (hexane and dodecane were used as solvents) using ruthenium-, platinum-, palladium, and nickel-containing catalysts based on metal nanoparticles stabilized in polymeric networks of hypercrosslinked polystyrene. All the synthesized catalytic systems were reduced in hydrogen flow at 300°C before the testing. During the catalytic testing the temperature, concentration of benzene and hydrogen pressure were varied. The catalyze content was studied by gas chromatography-mass spectrometry. The stability of synthesized catalytic systems as well as transformation of active metals on catalyst surface were studied by infrared diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, low-temperature nitrogen physisorption, and thermogravimetry. It was shown that the synthesized metal-containing systems remain stable during multiple repeated uses.

As a result of investigation it was shown that the polymeric matrix remains stable during the gas-phase reduction process. However, partial catalytic hydrogenation of aromatic rings of HPS takes place at the first catalytic cycle. During the further catalytic cycles, the transformations of polymeric matrix were not detected. Besides, the loss of catalytically active metallic phase during the reaction not occurred. It was also shown that for all the metals, the dependence of specific hydrogenation rate on temperature is bell-shaped.

Acknowledgments

This work was funded by the Russian Foundation for Basic Research (grant 16-08-00355).
The regularities of specific surface change, weigh of carbon black and propan-butane gas composition in the process of pyrocarbon formation are considered. Carbon black N234 was taken as a research object. The process of pyrocarbon formation was carried out at 650 °C and 700 °C.

It is established that carbon black specific surface area changing has peak of maximum [1]. In addition, decrease of weight increasing in the last stages of the process is observed. This is explained by the mechanism of pyrocarbon formation, which involves stages of condensation products formation in the gas phase and their deposition on the active centres. It is possible that decrease of weight increasing is associated with active centres blocking of black carbon and, as a consequence, fewer deposition of condensation products.

If it is really so, the condensation products must be carried away from the reactor by the gas flow. To capture these products at the reactor outlet filter was sated and fixed the change of its weigh in the empty reactor and with the sample of carbon black by weight of 0.05 g and 0.1 g.

The changing of the filter weigh in the empty reactor and with the portions of carbon black in the process of pyrocarbon formation

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Tar weight on the filter, g</th>
<th>Weigh of pyrocarbon, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Empty reactor</td>
<td>N234 (0,05g)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0,0263</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>0,1271</td>
<td>0,0042</td>
</tr>
<tr>
<td>50</td>
<td>0,2438</td>
<td>0,0161</td>
</tr>
<tr>
<td>70</td>
<td>0,3413</td>
<td>0,0302</td>
</tr>
</tbody>
</table>

Regardless of the weigh-loaded carbon black, a sharp decrease of the sample weigh is observed for the reactor with the sample of carbon black over the last 40 minutes process while increasing the weight increasing of the filter. We can assume that at the beginning of the process, the pyrocarbon deposition centers actively work and almost all the resulting condensation products intensively deposited on the surface of carbon black. By the end of the process some active centers is blocked by deposited pyrocarbon, because of condensation products does not have time to settle on the surface and carried away of the reactor precipitated on the filter. This is confirmed by studies conducted on the empty reactor, where the filter weigh is increased almost uniformly throughout the process. In this case we can speak about the simple thermal decomposition of hydrocarbon gas.

Thus, confirmed the hypothesis of pyrocarbon formation mechanism, implying the condensation products formation in the gas phase and their subsequent adsorption on the carbon substrate.

Reference:
THE UTILIZATION OF 2-(2-AMINOETHOX)ETHANOL IN THE SYNTHESIS OF NEW ORGANOSILICON PRODUCTS

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Organosilicon derivatives of alkohol amines are used as epoxy hardeners, oil wetting and dispersing agents, as well as preproducts for the preparation of special polymers.

We offer the method of 2-(2-aminoethoxy)ethanol organosilicon derivative synthesis, which involves silylation of 2-(2-aminoethoxy)ethanol (I) with the help of hexamethyldisilazane at a molar ratio of 2:1 in the presence of catalytic amounts of sulfuric acid.

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{Me}_3\text{SiNHSiMe}_3 & \xrightarrow{\text{H}_2\text{SO}_4} \text{H}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OSiMe}_3^- + \text{NH}_3 \\
\text{(I)} & \quad \text{(II)}
\end{align*}
\]

The process, which was carried out in one stage (reaction time was 8.5 hours) allowed to achieve target product yield (II) of 75%.

It is found out that the application of equimolar ratio of hexamethyldisilazane and alkohol amine does not result in production of silicon-derivative 2-(2-aminoethoxy)ethanol, containing O-Si and N-Si bonds (III), but ends, as in the first case, with production of (2-{2-[(trimethylsilyl)oxy]ethoxy}ethyl)amine (II).

The product was able to prepare only by reacting of (2-{2-[(trimethylsilyl)oxy]ethoxy}ethyl)amine with hexamethyldisilazane taken in molar ratio of 2:1.

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OSiMe}_3^- + \text{Me}_3\text{SiNHSiMe}_3 & \xrightarrow{\text{H}_2\text{SO}_4} \text{HNCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OSiMe}_3^- + \text{NH}_3 \\
\text{(II)} & \quad \text{(III)}
\end{align*}
\]

As in the first case the process was carried out in one stage (reaction time was 13 hours) with target product yield (III) of 50%.

Utilization of (2-{2-[(trimethylsilyl)oxy]ethoxy}ethyl)amine (II), prepared by reaction with phenylisocyanate allowed to produce previously unknown organosilicon urea – N-phenyl-N’-(2-{2-[(trimethylsilyl)oxy]ethoxy}ethyl)urea. The process was carried out without catalyst application and urea yield (IV) was about 100%.

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OSiMe}_3^- + \text{PhN}=&\text{C}=\text{O} & \xrightarrow{} \text{Me}_3\text{SiOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NHCNPh} \\
\text{(IV)}
\end{align*}
\]

Acknowledgements

The work was funded by State Order № 1984 "New polymer materials based on organic and organosilicon compounds, modified by carbonaceous fillers and metal oxides".
IMPROVING THE PROCESS OF DEWAXING PETROLEUM OIL

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In a multi-stage technology of petroleum oils up to 40% of total expenditure are accounted for dewaxing process. Therefore, the development of rational methods of increasing the efficiency of the process is a very urgent problem both from scientific and practical points of view.

In the industrial process technology of dewaxing raffinates are carried out under cooling materials in admixture with selective solvents. Suitable solvents are usually a mixture of the ketone (acetone or methyl ethyl ketone) and toluene. By varying the ratio of components in the solvent, this method can be used for any dewaxing feedstock fractional composition and viscosity at various temperatures and the process to obtain base oils with a wide solidification temperature range.

In this work, in order to reduce the cost of the process of dewaxing raffinates was tested instead of the ketone solvent is more affordable-isopropyl alcohol. Dewaxing was carried out according to known methods [1]. Dewaxing the raffinate was obtained by selective purification of N-methylpyrrolidone vacuum distillate VD-III (production of OJSC "Naftan"). Solvents compositions were acetone - toluene (60:40) and isopropyl alcohol - toluene (60:40). Solvent to feed ratio was 3:1 parts by weight. Results of the study are shown in Table.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dewaxed oil</th>
<th>Slack</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Output wt., %</td>
<td>nD&lt;sub&gt;50&lt;/sub&gt;</td>
</tr>
<tr>
<td>acetone - toluene</td>
<td>92,6</td>
<td>1,4764</td>
</tr>
<tr>
<td>isopropyl alcohol - toluene</td>
<td>96,0</td>
<td>1,4741</td>
</tr>
</tbody>
</table>

*) P = D<sub>720</sub>/D<sub>1465</sub> - the degree of paraffin; B = D<sub>1380</sub>/D<sub>1465</sub> - the degree of branching.

According to data provided in the table, the use of new solvent can increase the yield of dewaxed oil; increase its viscosity without changing substantially the dependence of viscosity on temperature. When this slack average molecule, selected from the raffinate, is characterized by a high degree of branching and paraffin.

**Reference:**
Direct catalytic conversion of vegetable oils (fatty acid triglycerides) into valuable hydrocarbon products, such as aromatic hydrocarbons is a perspective approach to obtain petrochemicals from renewable sources. High-silica zeolites and mesoporous aluminosilicates are active catalysts for the conversion of fatty acid triglycerides which allow to provide liquid hydrocarbon products of different structures.

We have synthesized and characterized by physicochemical methods MFI (ZSM-5) zeolites with a SiO$_2$/Al$_2$O$_3$ ratios 87, 40 and 136. The synthesis was carried out as a conventional hydrothermal (HT) and rapid hydrothermal-microwave (MW) methods. Methods of synthesis of silicalite MFI structure, containing no aluminum, and the MFI zeolite without template have also developed. It has been found that with the MW methods highly crystalline zeolite synthesis can be achieved in 3 hours. Zeolite with SiO$_2$/Al$_2$O$_3$=136 synthesized by MW method was obtained directly in the active H-form, without repeated ion-exchange with an aqueous ammonium nitrate (NH$_4$NO$_3$) which significantly reduce duration of synthesis. Alkaline treatment was carried out to form extra mesoporous structure. Some of obtained zeolites were modified by Zn, Cr, and Ga. Promotion of zeolites was carried out by a whiteness impregnation using aqueous nitrate solutions. XRD demonstrated that all synthesized zeolites are structural type of MFI, having characteristic peaks at 20 7-10 and 20-25°.

Catalytic properties of promoted and unpromoted zeolites were tested in hydroconversion of rapeseed oil (oil flow rate 3.0 $\pm$ 0.5 g / g cat h$^{-1}$, t = 600 $\pm$ 10°C) To compare, we tested industrial zeolite IK 17-1 with SiO$_2$/Al$_2$O$_3$ 33 called HZSM-5(P), produced by Novosibirsk Chemical Concentrates Plant. According to FT-IR spectroscopy, the conversion of rapeseed oil in all experiments was 100%.

Samples HZSM-5(MW)87, HZSM-5(MW)40 and HZSM-5(MW)136 showed comparable with HZSM-5(P) yield of aromatic hydrocarbons of 27-29%wt. On HZSM-5(HT)87 catalysts prepared by the traditional hydrothermal method we received a high yield of light olefins - 45% wt. The maximum yield of aromatic hydrocarbons - 49% wt showed catalysts synthesized by MW method with SiO$_2$/Al$_2$O$_3$ 87 promoted with Zn and Cr. In the hydroconversion of rapeseed oil on HZSM-(HT) with SiO$_2$/Al$_2$O$_3$ 40 without template and HZSM-5 silicalite a significant amount - 40 and 34% wt of liquid aliphatic hydrocarbons (up to C$_{11}$) was suddenly formed. It may be related to their special physical and chemical characteristics.

The results of this study point to the opportunity of widening the range of raw materials for the petrochemical industry by involving vegetable oils, as a renewable natural resource.

Acknowledgements
The research was financially supported by Russian Ministry of Education (Government contract “Organization of scientific research” profile number 1422, of the state task in the field of scientific activity № 4.306.2014/K) and RFBR (grants 14-03-31816 and 16-03-00273).
ENERGY SAVING DISTILLATION OF C4+ VAPOR CRACKING PRODUCTS

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Energy saving is an important problem in petrochemistry, especially in distillation. There are many publications devoted to this subject. Distillation is one of the most energy intensive and widely used separation methods in the chemical industry. In this reason, the distillation flowsheets are investigated of the hydrocarbons produced by vapor cracking (C4+ fraction). Partially thermally coupled distillation sequences and dividing wall columns (PTCDS) are proposed to separate the initial mixture of hydrocarbons and are compared with the traditional ones used direct (D) or indirect (I) separation. Industrial vapor cracking plants can use different raw fractions such as WLHF, ligroin, PBF, ethane etc. It leads to the differences of flowrates, compositions and concentrations of C4+ vapor cracking products and therefore to the difference of the energy consumption of different flowsheets. Seven different compositions are considered of the initial feed. In all cases the quality of the products are fixed.

In the case of different quantities of the initial feed, the relative energy consumption are used to compare the different flowsheets. Aspen Hysys is used to simulate distillation. Peng-Robinson equation is used to calculate VLE with the parameters from Aspen Hysys data base. Each flowsheet is optimized for each initial feed composition on the criteria of the energy consumption of boilers. PTCDS is synthesized by the algorithm [1]. Thus, 28 different variants are calculated and optimized. The efficiency of PTCDS implementations vs conventional distillation are shown in table. DQr=(Qr^con-Qr^PTCDS)/Qr^con*100%; DQc=(Qc^con-Qc^PTCDS)/Qc^con*100%; where Q – energy consumption, con – conventional distillation sequence, c – condenser, r – boiler.

<table>
<thead>
<tr>
<th>Feed composition</th>
<th>PTCDS D vs conventional two column distillation system D</th>
<th>PTCDS I vs conventional two column distillation system I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DQr(%)</td>
<td>DQc(%)</td>
</tr>
<tr>
<td>1</td>
<td>14,66</td>
<td>9,08</td>
</tr>
<tr>
<td>2</td>
<td>13,19</td>
<td>8,47</td>
</tr>
<tr>
<td>3</td>
<td>4,71</td>
<td>3,64</td>
</tr>
<tr>
<td>4</td>
<td>14,47</td>
<td>8,33</td>
</tr>
<tr>
<td>5</td>
<td>13,80</td>
<td>7,72</td>
</tr>
<tr>
<td>6</td>
<td>13,31</td>
<td>6,87</td>
</tr>
<tr>
<td>7</td>
<td>5,40</td>
<td>2,34</td>
</tr>
</tbody>
</table>

The results give an ability to optimize traditional distillation by the implementation of PTCDS at the petrochemical plants.

Reference:
CURRENT STATUS AND THE IMPROVEMENT OF PRODUCTION OF CYCLOHEXANONE

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Cyclohexanone (CH-one) is widely used in the manufacture of polyamide plastics and synthetic fibers such as nylon-6 and nylon-66. In the industry CH-one is mainly produced by liquid phase oxidation of cyclohexane (CH) in the presence of a catalyst. A significant disadvantage of this method is extremely low (about 4%) conversion of hydrocarbon and selectivity (~ 75-80%) on useful products, including cyclohexyl hydroperoxide and cyclohexanol (CH-ol). Low extent of transformation of CH in oxidation reactors leads to increase of energy consumption at recycling of CH.

According to the existing facilities, the ratio CH-ol : CH-one in oxidation products is about 2 : 1, and additional steps of separation of reaction mass and dehydrogenation of alcohol to the ketone is required.

Thus, the presence of multiple stages and high power consumption reduces the efficiency of the "oxidative" method of obtaining CH-one, thereby holding back the further growth of its production. In this regard search of ways of improvement of production of CH-one with approbation of new technologies in the petrochemical industry is an important task. The scientific researches executed by us, which results are given below, have been directed to the solution of this task.

Scientific and applied aspects of a method of joint receiving phenol and CH-one on the basis of the benzene including synthesis of cyclohexylbenzene (CHB) via benzene hydrodimerization, liquid-phase oxidation of CHB to hydroperoxide and acidic decomposition of the last into target products, according to the scheme, are developed:

The catalysts of CH oxidation, that allow to increase its conversion by 2-3 times and cumulative selectivity of CH-ol and CH-one formation over 90% has been proposed and experimentally approved.

The offered catalysts give the chance to carry out liquid-phase oxidation of CH-ol into CH-one at conversion of CH-ol of 45-50%.

The heterogeneous catalyst of dehydrogenation of CH-ol in CH-one providing conversion of alcohol of 50-57% and selectivity of formation of ketone more than 99.6% is developed and introduced in production on JSC Shchekinoazot.

Results of researches and the analysis of efficiency of possible application of the above-stated methods of industrial synthesis of CH-one are given in this work.
Nowadays the topic of associated gas utilization is as relevant as ever. About 150 BCMPA of it is still flared worldwide. This problem has a serious ecologic and economic consequence. However, the gas could be convert into synthetic fuel by gas to liquid technology, mixed with crude oil and thus monetized. Alternatively, it could be convert into methanol and used as hydrate growth inhibitor. Both this technologies belong to so-called C1 chemistry, what means that they proceed through the stage of synthesis gas (mixture of hydrogen and carbon monoxide) formation.

Main issue of such a solution is that they are not cost effective, so it is cheaper to flare all the gas. The latest work of different companies reduce break-even point of the synthesis stage. However, the stage of syngas formation comprise more than a half of the total CAPEX of the plant.

Traditional industrial reforming processes are steam methane reforming (SMR), two step reforming and autothermal reforming (ATR). Thermal partial oxidation (POX) is a promising technology for reforming of methane to produce syngas – mixture of hydrogen and carbon monoxide that is source gas to C1 processes.

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2 + 35,6 \text{ kJ/mol}
\]

POX has a number of advantages in comparison to ATR and SMR. They are – relatively simple and small reactor, absence of necessity in heat supply or catalyst and hydrogen to carbon monoxide ratio that principally fit the requirements of methanol and gas-to-liquid processes. However, this technology also has its drawbacks that are soot formation and low hydrogen yield.

The only application of POX in chemical technology up to date are big Shell GTL plants. The reason of that is a high price of air separation units. That is why POX was the technology of choice only when economy of scale is achieved. Nevertheless, nowadays oxygen penetrating ion exchanging membrane (IEM) technology become available. For the work ITM need heat – temperature about 1000 °C, what could be provide by exothermic POX reaction. Potentially that could make GTL cost effective at the price of crude oil below 20 $/b and make utilization of associated gas cost effective.

The aim of this work was to optimize controlling parameters of the system and to reach the steady state of the process in combination of high yield of syngas and high conversion of source gas. In particular, target objective is to create such a system that would produce syngas for Fisher-Tropsh synthesis that would not require any purification stage.
THE DEOXYGENATION CHEMISTRY OF STEARIC AND OLEIC ACIDS OVER NICKEL SULFIDE CATALYSTS

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Scientific and technological efforts at the beginning of the 21st century had a target to develop and study the methods of industrially producing hydrocarbon fuels based upon renewable sources (RNS) of natural inedible fats and oils as well as the waste products of their edible ones. This resulted in the creation of four synthetic kerosene and diesel production plants with 1.5 million tons sum capacity. They utilize a technology based on hydrodeoxygenation (HDO) of triglycerides and free fatty acids. The main progress is that this “green fuel” contains no oxygen unlike biodiesel and biokerosene.

Selective production of higher olefins (HOs) is an actual problem too, because they are large-tonnage important key reagents of industrial organic syntheses. HOs form partly during HDO and are the primary products of fatty acids decarbonylation (DCO). They completely transform into paraffins during fuel production. Hence, the problem is to search for a proper catalyst providing high reaction selectivity to HOs. Stearic (St) and oleic (Ol) acids are prevailing components of above mentioned RNS, and therefore used as the relevant model substances.

A literature search has revealed that metal sulfides, and especially Ni, are promising catalysts for this purpose [1]. They usually formed by sulfidation of Ni oxide and remained in this form by continuous injection of sulphiding substance into feed flow. We prepared Ni sulphide catalysts supported on alumina or silica by hydrogen reduction of Ni sulphate as the precursor. These catalysts as distinct from known Ni and Ni sulphide containing ones appeared to have relatively low side activities.

The hydrogenation type reactions in their presence are minor. Ol does not practically form St. Moreover Ol does not inhibit the conversion, and the figures for St, Ol and their mixtures are close to those for pure St. C_{17} diolefins (DCO primary products of Ol) partially convert to C_{17} olefins. C_{18} hydrocarbons (HDO products) do not form. Methane (a product of CO methanation) is absent. The selectivity to heptadecane is less then 10%. The shift reaction is practically absent. Ester and ketone products present only in traces.

In this case, the heptadecenes’ oligomerization is the main side reaction. Overcoming its consequences is an actual problem. It partly becomes simpler by the ability of metal catalysts to inhibit the oligomerization of olefins in the hydrogen presence [2]. With the catalyst 3.2% by Ni on silica at 98% St conversion level, we obtained heptadecenes yield of 40%. This figure may sharply rise by increasing the catalyst loading as well as by using the well-known technological trick – simultaneous heptadecenes removal from the reaction zone.

Acknowledgements
The RFBR financially supported this study, projects 15-03-02906 and 14-03-00105.

References:
DECOMPOSITION OF ORGANIC MATERIALS UNDER ELECTRIC DISCHARGES ACTION

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Electrical cracking process can be considered not only as a source gas, containing acetylene and hydrogen, soot and soot-containing paste, but also as a way of utilization various industrial liquid organic wastes of chemical and petrochemical manufactures. In this case decision of ecological problem - waste utilization will be accompanied by decision of another one – waste will be considered as secondary raw materials.

Research of electrical cracking process was carried out with gasoline, kerosene, diesel and oil petroleum fractions, as well as waste, which were presented by alcohol-ether, ether, butyl-benzene fractions provided by ZAO «Sibur-Khimprom».

It is shown that with increasing degree of raw material decomposition, the concentration of acetylene in the gas increases. It should be noted that increasing in the degree of raw materials decomposition leads to differences leveling in the gas composition obtained from the related factions.

Gas composition changing associated with the transformations taking place in the liquid phase in the process of its expansion. These transformations are characterized by increasing in the values of the refraction index and the density of the liquid phase. Such kind of parameters changes of the liquid phase show that increasing in conversion degree of raw materials is accompanied by its composition changes in the hydrocarbon group, namely by alkanes number reduction and arenes content increasing, i.e. the degree of materials aromatization increases.

Increasing the degree of materials aromatization promotes the soot yield increasing.

The table shows the characteristics of some soot samples.

### Influence of process conditions on soot obtained characteristics

<table>
<thead>
<tr>
<th>Index</th>
<th>Raw materials</th>
<th>Gas production, l/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Average particle diameter, nm</td>
<td>Gasoline fraction</td>
<td>23,3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gasoline fraction</td>
<td>27,5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Specific adsorption surface, m²/g</td>
<td>Gasoline fraction</td>
<td>306</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gasoline fraction</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>The ultimate degree of pores filling</td>
<td>Gasoline fraction</td>
<td>191</td>
</tr>
<tr>
<td>with pyrolytic carbon, %</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gasoline fraction</td>
<td>244</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

It is seen that increasing the gas production results in a reduction of the specific surface, increasing the diameter of the soot particles and the ultimate degree of pores filling with pyrolytic carbon. Last index characterizes soot structuring.
Epichlorohydrin is an important product of basic organic synthesis. Due to the presence of two reaction sites in the molecule, it easily reacts with organic compounds of different classes. It is used for production of a number of compounds used in many industries. At present there are several commercially viable technologies of epichlorohydrin production. One promising direction of epichlorohydrin manufacturing is the liquid-phase epoxidation of allyl chloride with an aqueous solution of hydrogen peroxide in methanol medium in the presence of a heterogeneous catalyst. In this work we have studied the structure of the phase equilibrium diagram of the multicomponent mixture of epichlorohydrin production according to this method. Based on this research, we have developed the separation scheme of the reaction mass to yield the required purity epichlorohydrin.
The activity of heterogeneous catalysts is associated with the size of the active phase clusters. According to the author, the main reason is not the size of the cluster but defects in the crystal lattice which arise at the interface of the crystallites active component of the catalyst. Therefore, it will be correct to compare the heterogeneous catalyst activity not with the cluster but with the crystallite sizes. Correlation between the crystallite size and catalytic activity appears in the catalytic reactions with inflicted and processed catalysts and in non-catalytic processes, such as pyrolytic carbon deposition or black carbon oxidation.

The reason of that lies in the fact that as for catalytic reactions but also for pyrolytic carbon formation or carbon materials oxidation the chemical interaction act follows by stage of reagent adsorption on the surface of the solid phase. Adsorption occurs on the solid phase crystal lattice defects arising at the boundaries of its crystallites contacts.

This report presents the research results of the pyrolytic carbon coating processes, its oxidation by carbon dioxide and air, synthesis of carbon nanofibers of carbon monoxide and hydrocarbons. In all cases, an increase in crystallite size of the solid phase (reducing extent of their contact boundaries, and thus the number of defects) decreased the rate of chemical reaction. In case of carbon nanofibers synthesis changes in crystallite size were also accompanied by diameter changes of formed nanofibers.

Some results that confirm the relationship between the boundaries length of carbon crystallites contacts and reaction rates of its pyrolytic carbon coating and oxidation are shown in a Table.

**The effect of carbon crystallite size on the rate of reactions taking place on its surface**

<table>
<thead>
<tr>
<th>TC mark</th>
<th>The length of the crystallites contacts borders, nm</th>
<th>The initial formation rate of pyrolytic carbon <em>10^2, mg/min</em>m^2</th>
<th>The rate of oxidation *10^2, mg/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>N220, subjected to preliminary graphitization</td>
<td>1200</td>
<td>1,94</td>
<td>15,2</td>
</tr>
<tr>
<td>N234, subjected to preliminary graphitization</td>
<td>1700</td>
<td>4,10</td>
<td>36,1</td>
</tr>
<tr>
<td>N375</td>
<td>2000</td>
<td>-</td>
<td>36,2</td>
</tr>
<tr>
<td>N220</td>
<td>2900</td>
<td>9,10</td>
<td>78,6</td>
</tr>
<tr>
<td>N234</td>
<td>4300</td>
<td>13,90</td>
<td>88,1</td>
</tr>
</tbody>
</table>
Halogenated organic waste has strong toxicity affect on the environment. That is reasons why chemical industry should do waste recycling of organohalogen compounds. This goal can be reached, for example, by controlled high-temperature incineration, fume incineration and regenerative thermal oxidation. Nevertheless the main deficiency of this process is high temperature, which usually occurs could be used on the order of 1000-1200 °C. The solution was used the catalytic oxidation. This process to be requires much lower thermal conditions, typically in the range of 300-500 °C.

It is known that combined catalysts based on cooper and vanadium are used either for the oxidation of CO to CO₂, methane oxidation or ethylene oxidation and total oxidation of hydrocarbons.

This paper examines the influence of CuCl-V₂O₅/Al₂O₃ based catalyst on the oxidation of chlorobenzene. It was synthesized via hydrothermal synthesis in homogeneous precipitation conditions. The carrier was precipitated in aqueous-alcoholic solution of NH₄Cl. The carrier was coated by copper chloride and vanadium oxide via penetration method. Aluminium oxide was soaked in ammonia solution of CuCl; the concentrations of the solution were 2.5 and 4 wt. %. Desiccation of the catalyst was carried out by slow heating to 110 °C on air for 5 hours. In the beginning the calcinations was carried out at temperature of 200 °C for 3 hours, then temperature was risen to 400 °C and kept for 5 hours. The concentration of copper cation in the catalyst was defined via atomic absorption spectrometry. Next, the CuCl/Al₂O₃ was soaked in water solution of NH₄VO₃, the concentrations of the solution were 2.5 and 4 wt. %. Desiccation of the catalyst was carried out by slow heating to 110 °C on air for 5 hours. The calcination was carried out at temperature of 600°C for 5 hours. The content of V⁵⁺ in the catalyst was defined via titrимetry.

Chlorobenzene oxidation starts at the temperature above 300 °C (1.0 and 5.8%), whereas thermal decomposition of chlorobenzene under the above-indicated experimental conditions on Al₂O₃, as well as in the reactor without catalyst, is observed only at temperatures exceeding 400 °C. Conversion of chlorobenzene on catalyst 2.5% CuCl-2.5% V₂O₅ / Al₂O₃ was almost up 90% at 500 °C, selectivity for CO₂ was 58% and above 90 % at 400 °C (selectivity for CO₂ was 47%) on 4% CuCl-4% V₂O₅ / Al₂O₃.

In chlorobenzene transformation products, other than CO₂, we identified by gas chromatography-mass spectrometry derivatives of chlorobenzene in trace amounts. Perhaps these products are formed by a reaction of chlorobenzene disproportion.

Acknowledgements
This work had been performed with financial support of RFBR, project N 14-03-00630_a.
ENERGY SAVING TECHNOLOGY OF RECTIFICATION BENZENE-TOLUENE-XYLENE’S FRACTION IN COMPLEXES WITH PARTIALLY CONNECTED THERMAL AND MATERIAL STREAMS

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Multicomponent organic products distillation is one of the most energy intensive processes in the chemical and petrochemical industries. Technological schemes of benzene-toluene-xylenes fraction (BTX) distillation was an object of the investigation. Research with receiving individual products are considered. Traditionally, this fraction is separated in the conventional two-column sequence.

Recently the attention of researchers is attracted by the fully (FTCDS) and partially (PTCDS) thermally coupled distillation systems. They increase a distillation thermodynamic efficiency and usually decrease in specific energy consumption.

The aim of this research is to compare different distillation schemes, and find the best on the criteria of minimum energy consumption. Four different schemes have been considered to solve the problem, including two traditional schemes and two PTCDS. PTCDSs were synthesized by algorithm [1].

Aspen Hysys was used for simulation. Vapor-liquid equilibrium was simulated by Peng-Robinson equation with Aspen Hysys database parameters. Individual schemes were optimized on the feed plate locations and for PTCDS on the value of the interconnected streams. The obtained data are presented in Table: \( N_{F1}, N_{F2} \) – the number of the feed plate in the first and the second columns, \( q \) – the energy consumption of the reboiler (r) and condenser (c) of the individual column, \( Q \) – the reboilers energy consumption of the schema.

The heat duties of condensers and reboilers for the conventional two-column sequences and PTCDS (Direct and Indirect)

<table>
<thead>
<tr>
<th>Scheme</th>
<th>( N_{F1} )</th>
<th>( q_{1c} ) (kW)</th>
<th>( q_{1r} ) (kW)</th>
<th>( N_{F2} )</th>
<th>( q_{2c} ) (kW)</th>
<th>( q_{2r} ) (kW)</th>
<th>( Q_c ) (kW)</th>
<th>( Q_r ) (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17</td>
<td>1807</td>
<td>1200</td>
<td>20</td>
<td>949</td>
<td>958</td>
<td>2756</td>
<td>2158</td>
</tr>
<tr>
<td>2</td>
<td>17</td>
<td>1675</td>
<td>0</td>
<td>23</td>
<td>878</td>
<td>1953</td>
<td>2553</td>
<td>1953</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1774</td>
<td>1155</td>
<td>19</td>
<td>1575</td>
<td>1595</td>
<td>3349</td>
<td>2750</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0</td>
<td>1164</td>
<td>21</td>
<td>2586</td>
<td>823</td>
<td>2586</td>
<td>1987</td>
</tr>
</tbody>
</table>

The PTCDS decrease energy consumption of reboilers and heat duties on the condensers. It is established that the PTCDS synthesized on the base of direct separation obtains the minimum value of the energy consumption, it is better than the best conventional schema up to 9.5%.

Reference:
PREDICTING THE YIELD OF PROPANE-PROPYLENE AND BUTANE-BUTYLENE FRACTIONS DURING THE CATALYTIC CRACKING PROCESS

Shafran T.A., Nazarova G.Y., Stebeneva V.I.

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The technology of catalytic cracking (CC) is a universal method of heavy hydrocarbon processing. A high-octane gasoline and light olefins (C3-C4) are the valuable products of CC process and also the valuable feedstock for the petrochemical industry.

The prediction the yield of gasoline fraction and the content of PPF and BBF (propane-propylene and butane-butylene fraction) at wet gas composition during the operation of two samples of cracking catalyst using the mathematical model is the purpose of this research.

The object of research are industrial cracking catalysts (CAT-1 and CAT-2) used at the catalytic cracking units, that are the part of KT-1/1 - the combined unit of deep processing of vacuum resid. The CAT-1 zeolite catalyst characterized by a high content of zeolite components (Y and ZSM-5) - 31.5 and 12.0 wt.%, relative to the CAT-2 catalyst (2 and 20 wt.%). The ratio of zeolite ZSM-5 to Y is 0.381 for the CAT-1 catalyst and 0.11 for the CAT-2 catalyst.

The mathematical model of CC process based on a formalized scheme of hydrocarbon conversion was used for the task. The model was complemented by the cracking reactions of paraffins, isoparaffins and olefins with formation BBF, PPF, gas components in order to predict the products yield from CC unit, group composition of products, octane number of gasoline, the content of PPD and BBF at wet gas.

The calculations were performed at constant process conditions (catalyst temperature at the regenerator outlet is 690°C, feedstock flow rate is 378 m³/h, feedstock temperature is 304°C, the slurry flow rate to the reactor is 9.2 m³/h, the steam flow rate for feedstock routing is 2400 kg/h, the steam flow rate for creating upward flow is 5500 kg/h, the catalyst circulation rate is 5.56 tₙₑₙₜₗₜₑ₃₉₉/ₖₖₙₜₑ₃₉₉₉, and at constant feedstock composition (the ratio of saturated hydrocarbons to aromatic hydrocarbons in the vacuum distillate is 2.1, the content of alcohol-benzene resins is 3.5 wt.%, feedstock density is 0.904 kg/m³).

The yield of wet gas was 38.53 wt.% during CAT-1 catalyst operation, for the reason of high selectivity of secondary cracking reactions with transforming of gasoline fraction hydrocarbons to wet gas, and 16.8 wt.% for CAT-2. The yield of gasoline fraction for CAT-1 amounted to about 40.61 wt.% and 58 wt.% for CAT-2. The composition of wet gas for CAT-1 is characterized by a high content of PPD (37.07 wt.%), against 31.50 wt.% for CAT-2 (due to low content of ZSM-5 zeolite). The content of BBF for CAT-1 and CAT-2 is 31.50% and 34.35 wt.%, respectively.

The gasoline fraction is characterized by a high content of olefins (19.53 wt.%), during CAT-2 catalyst operation, because the olefins from gasoline less cracking with gases formation (due to low content of ZSM-5 zeolite). The content of aromatic hydrocarbons in gasoline during CAT-1 catalyst operation is significantly higher (42.36 wt.% - CAT-1 and 34.29 wt.% - CAT-2), for the reason of high rate of aromatic hydrocarbons dealkylation and olefins aromaticization (high content of Y-type zeolite).

The high content of aromatic hydrocarbons in gasoline from CAT-1 provides the high octane number (93.8 p.). The contents of isoparaffin hydrocarbons in gasoline during CAT-2 catalyst operation higher, due to high rate of hydrogen redistribution reactions. Octane number is 91.35 p.

Using the mathematical model CC process allows to estimate the effect of catalyst cracking composition on the distribution of main products of the process, the content of PPF and BB at wet gas, the gasoline composition and octane number.
EFFICIENT AND SELECTIVE COUPLING OF CARBON DIOXIDE AND 1,2-EPOXYCYCLOPENTANE CATALYZED BY CoCl₂-QUATERNARY AMMONIUM SALT SYSTEM

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In the modern chemical industry an important task is the efficient use of by-products of current large-scale production plants. The C₅-fraction of pyrolysis containing up to 15% of cyclopentene is one of them. The oxidation into 1,2-epoxycyclopentane, which has its own application and is used in the synthesis of oxygenated derivatives of cyclopentene: 1,2-cyclopentanediol, cyclopentanol, cyclopentanone, δ-valerolactone, glutaric acid, etc., can be distinguished among the most rational ways of cyclopentene’s using.

In recent years, increasing attention is attracted to cyclopentene carbonate obtained by coupling 1,2-epoxycyclopentane and carbon dioxide:

\[
\text{1,2-epoxycyclopentane} + \text{CO}_2 \rightarrow \text{cyclopentene carbonate}
\]

Growing demand for this product is explained, on the one hand, by its highly valuable properties of the effective solvent and extractant and, from the other hand, the ability to use it for obtaining of a urethane polymers, that have heightened strength and biodegradability, by environmentally-friendly, non-isocyanate technology. In addition, the cyclopentene carbonate synthesis can be the way of carbon dioxide recycling on a industrial scale. It can help to find the solution for the global environmental problem of the greenhouse effect.

The carboxylation of C₃-C₁₆-aliphatic, C₆-, C₈-, C₁₂-alicyclic and natural epoxides are detailed in the literature. However, it is noted, that the coupling of cyclopentene oxide with CO₂ is carrying out with a low rate or absents. Selectivity of cyclopentene carbonate is not higher than 45-47%, in the presence of the proposed catalysts.

We have tested catalysts, e.g. halides of alkali metal, of quaternary ammonium salts and of transition metals, that are used for industrial synthesis of alkylene carbonates: So, the reaction was carried out in the presence of the solvent (DMF, THF) or without it. Halides of cobalt, of chromium, of nickel and tetraethylammonium bromide (TEAB) were the most active among others. We had achieved complete conversion of the epoxide, but the selectivity of cyclopentene carbonate did not exceed 80% in presence of these catalysts.

It is known that the ability of quaternary ammonium salts to form complexes with transition metal halide is used at creating and modeling catalysts for isomerization and oxidation of olefin. Besides high efficiency, these catalyst systems are soluble in epoxides. It gives an opportunity to carry out the synthesis without solvent. CoCl₂ or CrCl₃, that were combined with TEAB, were the base of complex systems, that we had tested. The researches had proven that CoCl₂-TEAB was the most efficient catalyst system for carrying out the carboxylation reaction of 1,2-epoxycyclopentane. The conditions, that were found by us, pvide the selectivity of cyclopentene carbonate, which is not less than 98%, and complete conversion of the epoxide after 4 h of experiment.

Cyclopentene carbonate was separated by vacuum rectification with a purity of 98.5%. It was found that one isomer - only cis-cyclopentene carbonate, is produced in the presence of the selected catalyst system.
Increasing in the depth of processing of heavy petroleum fractions is a major task of refining industry. It can be achieved by raw material modifying with mechnanochemical activation (MCA) using apparatus of various designs and unconventional influence principles on the raw materials.

The aim of this work is the study of influence of mechanical activation on the heavy oil fractions.

The fuel oil was used as the raw material (F1o, F2o) with the following characteristics: density - 963,4 and 956,0 kg/m³; boiling point – 230 and 262 °C; fractions content: bp-350 °C - 13,23 and 1,73 % mass., 350-480 °C - 58,47 and 16,77 % mass., >480 °C - 23,96 and 77,22 % mass. respectively.

MCA of fuel oil was carried out on the high pressure disintegration unit DA -1. The apparatus construction supplies raw material from the storage container into the high pressure chamber and through a dispersing head into the receiving tank. During the treatment the cavitation phenomenon appeared and led to the destruction of petroleum hydrocarbons into simpler components. MCA was carried out at a pressure of 20 MPa and 5 cycles (cycle - raw material pass through the dispersing head).

As a result of MCA was obtained fuel oil (F1MCA, F2MCA) with the following characteristics: density - 963,0 and 949,0 kg/m³; boiling point – 208 and 234 °C; fractions content: bp-350 °C – 16,36 and 2,54 % mass., 350-480 °C – 60,25 and 27,22 % mass., >480 °C – 16,51 and 61,80 % mass. respectively.

After treatment the fraction content boiling above 480 ° C reduced with increasing the part of lighter fractions. This observation with decreasing in the density indicates occurring degradation of high boiling oil components with forming hydrocarbons of lower molecular weight.

The following table shows the content of normal alkanes and alkanes of isoprenoid structure in F2o and F2MCA fuel oil.

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>Content in fuel oil, %</th>
<th>original</th>
<th>converted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes C7-C15 (b.p. 98-271 °C) including iso- C14/iso- C15</td>
<td>4,80</td>
<td>8,37</td>
<td></td>
</tr>
<tr>
<td>Alkanes C16-C32 (b.p. 287-475 °C) including iso- C19/iso- C20</td>
<td>64,45</td>
<td>49,65</td>
<td></td>
</tr>
<tr>
<td>n-alkanes C33-C40 (b.p. 484-540 °C)</td>
<td>6,51</td>
<td>4,65</td>
<td></td>
</tr>
<tr>
<td>Summary alkanes, including isoprenoids</td>
<td>75,76</td>
<td>62,67</td>
<td></td>
</tr>
<tr>
<td>Representatives of other classes</td>
<td>3,43</td>
<td>3,13</td>
<td></td>
</tr>
<tr>
<td>∑ C7-C15/∑ C16-C40</td>
<td>100,00</td>
<td>100,00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0,07</td>
<td>0,15</td>
<td></td>
</tr>
</tbody>
</table>

Thus, under the cavitation influence the destruction of the dispersed structure oil, partial cracking of alkyl chains and the formation of relatively low molecular weight alkanes (C7-C15) and other classes of compounds are occured.
CORRELATION BETWEEN YIELD OF FUEL DISTILLATES AND COMPOSITION OF COMPOUND OIL FEEDSTOCK

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Oil compounds of various fractional and chemical compositions are widely used as a feedstock at oil refineries. Compounds are often formulated without taking into account special characteristics of merged streams. Meanwhile, it was shown experimentally, that disperse systems, formed during mixing, in number of cases change their properties in multi extremum and non-additive way, depending on proportion between mixed products [1, 2].

Such basic properties of compounds as density, viscosity, pour point, surface tension etc. at first depend on characteristics of disperse systems of mixed oils. In laboratory conditions, determination of fraction composition is performed by distillation, e.g., by gradual evaporation method. This process requires heating, which is followed by both appearance of vapor phase and thermolysis of molecules with high boiling point in condensed media. Thermolysis, as well as low precision of fractions separation, leads to change in fraction composition, formed right after mixing of oils.

In our research we used different methods for determination of physical properties of oils and their binary mixtures of various compositions (density, kinematic viscosity, pour point). Specified correlation between indicated properties and proportion of mixing components allows considering possibility and conditions of merged pipeline transport.

In order to obtain more precise fraction composition of oils and their mixtures, we used simulated distillation – chromatography method for determination of components by boiling temperatures range (GOST R 54291-2010). Based on results of simulated distillation we made curves of true boiling temperatures (ITK), determined potential content of fuel fractions in mixtures and selected optimal composition of compounded feedstock, which met requirements for yields of distilled key fractions: IBP - 150 °C, IBP - 180 °C, 150 - 250 °C, 180 - 320 °C, 250 - 320 °C.

We consider that more reliable forecast of potential content of distillate fractions in compounds can be achieved, provided that correlation between ITK curves will be taken in account during selection of optimal composition of compound, in addition to physical and chemical properties of oils.

Acknowledgements
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References:
SYNTHESIS OF NEW MONOMER FOR SULFONATED POLY(ARYLENE ETHER SULFONES)
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One of the most promising classes of aromatic condensation polymers for making proton-conducting membranes for fuel cells are sulfonated poly(arylene ether sulfones) (HSO₃-PAES), having high proton conductivity values. Preparation the latest from sulfonated monomers is more preferred than the approach of the subsequent introduction of protogenic groups in a polymer-analogous transformations, since it allows to obtain a strictly ordered structure of the polymer and a certain amount of protogenic groups.

New monomer has been proposed for making a new and effective proton membranes - 4-({2,4-bis-[(4-chlorophenyl)sulphonyl]phenyl}thio)benzenesulfonic acid (DCIDS-SO₃H). The following data were taken into account in its molecular design:

- A big molecular weight of the aromatic sulfone, and the presence of two high reactive reaction centers for the reaction of aromatic nucleophilic substitution will allow to the production of high molecular weight polymer;
- Protogenic group should be in a pendant chain, since its presence in the polymer chain can increase the fragility of the resulting coating films. Therefore, for the introduction of sulfonic monomer moiety, it is necessary to have high reactive center for electrophilic substitution;
- It is desirable that the side group has been linked with the main chain via bridging atoms or groups that have reduced rigidity of macromolecules and improve their solubility;
- The presence of two sulfonic groups in an elementary unit should improve the stability of the polymer material to the oxidising agents;
- Polymers whose backbone consists of meta-substituted moieties are processed better in a polymer film.

The synthesis of the new monomer DCIDS-SO₃H represented on the scheme:

![Synthesis Scheme](image)

New and efficient synthetic technique was developed which allows obtaining the desired product in high yield and purity. The structure of all intermediates and the monomer was established by ¹H NMR techniques, ¹³C NMR spectroscopy, high resolution mass spectrometry, and elemental analysis.

**Acknowledgements**
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THE RESULTS OF STUDIES ON INDICATOR UNIQUENESS OF TENDENCY TO FORM DEPOSITS IN THE GASOLINE INJECTORS PRODUCED IN THE APPARATUS OSV-1

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In developing non-motorized methods for evaluating operational properties of petroleum, oil and lubricants (POL) there are two main problems: the adequacy of the results obtained in relation to the real operating conditions and the uniqueness of the proposed evaluation criteria (i.e. the inability to assess this index as a result of the existing evaluation methods). One of the most actual operational properties indicator of automotive engine fuel, at present, is a tendency to form deposits in the injection system of gasoline engines. The bulk of modern spark-ignition engines are fitted with fuel injection system. Thus the main factor that has an impact on the injection parameters degradation of a modern gasoline engine in operation is the fouling of nozzles.

A method based on the analysis of deposit formation patterns on the fuel injectors of gasoline engines implemented in the apparatus OSV-1 [1] was developed in the FAE «The 25th State Research Institute of Himmotology of Ministry of Defence of the Russian Federation». An indicator of the tendency of motor gasoline to the deposit formation is a visual score of the optical density (darkening) of nozzle bottoms. Studies have shown that this indicator has a range sufficient for differentiation of commercial gasoline. The adequacy of the results obtained in relation to the real operating conditions can be evaluated upon the results of the fuel injector fouling assessment using standardized in WWFC methods (bench test procedure ASTM D 6421 and vehicle test procedure (10 000 miles) ASTM D5598). These studies are planned by the authors to the implementation on the second stage of research, but are beyond the scope of this work.

In this paper it was been studied the resulting evaluation criterion in terms of its uniqueness and independence from existing indicators. For this purpose 45 samples of commercial automotive gasoline of various grades and manufacturers were tested in the apparatus to determine the rate of injector fouling according to the developed method. Further for each fuel sample indicators were determined, which, in our opinion, could have influenced the fouling rate of fuel injector: the volume fraction of aromatics and olefins (GOST R 52063), the amount of oxidation products [2], the share of absorbed oxygen [3], the tendency to form deposits in the intake system [4], the concentration of existent gum (GOST 1567).

Studies have shown absence of correlation between the parameters above and characteristics, resulting in the installation OSV-1. Thus it can be concluded, that this indicator is unique, it does not depend on the existing standard indicators.

References:

STABILITY OF METAL-CONTAINING CATALYTIC SYSTEMS
BASED ON HYPERCROSSLINKED POLYSTYRENES
IN REACTIONS OF LIQUID-PHASE HYDROGENATION

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Modern heterogeneous metal-containing catalysts are based on inorganic supports, e.g. activated carbon, ceramics, silica, alumina, titania, wide pore and narrow pore zeolites. However, according to the data of recent studies, high activity and selectivity of processes of partial hydrogenation and oxidation can be achieved while using the same active phases stabilized by polymers. Among the polymers, block-copolymers forming micelles, hydrogels, dendrimers, and also crosslinked polymeric networks can be used as catalytic supports. Reasonable activity and high selectivity of polymer-based catalysts containing palladium, platinum and ruthenium was shown in a number of industrially important liquid-phase hydrogenation (of dehydrolinalool, nerol, dimethyl ethynyl carbinol, D-glucose, ethyl pyruvate and of substances containing amide bond) and oxidation (of phenols, 2-methylnaphthalene and L-sorbose) processes. In many cases, activity and selectivity was shown to be noticeably higher in the presence of polymer-based catalysts in comparison with the industrial catalysts based on inorganic supports. Synthesis of such metal-containing catalysts is based on a concept of metal nanoparticle formation in microcavities already existing or being formed in polymeric system. In this work the pores of polymeric matrix of hypercrosslinked polystyrene (HPS) were used as microcavities for nanoparticle formation. It is noteworthy that stabilization of metal particles in HPS is due to both electron and steric effects.

Conditions of partial hydrogenation and oxidation using HPS-based catalysts can be strongly varied depending on the substrate: temperature range of 60-180°C, hydrogen/oxygen partial pressure up to 10 MPa. Thus the search of the limits of stability of the polymeric matrix (commercial polystyrenes of MN100 and MN270 types were used as supports) as well as metal-containing (Pt, Pd, Ru) catalytic systems was the aim of this work. In this study, the completeness of metal reduction and stability of used polymers in the process of catalyst syntheses and further reduction and also during the catalytic testing were determined.

Stability of HPS-based catalytic systems and transformations of active metal phase on the catalyst surfaces were investigated by the method of infrared diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, low-temperature nitrogen physisorption, and thermogravimetry and transmission electron microscopy.

The used polymeric matrices were shown to remain stable at a temperature up to 300 °C and even higher during the process of gas-phase reduction of active metals from precursors. Besides, HPS changes only slightly during the catalytic testing. Based on the data of XPS and TEM study, it was shown that formation of catalytically active phase and its migration inside the polymer takes place not only during the reduction process but also during the catalytic experiments.

Acknowledgments
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STUDY OF MICROBIOLOGICAL ACTIVITY OF AROMATIC ACETYLENE ALCOHOLS OF THE OIL AND GAS INDUSTRY

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Influencing ketones and aldehyds on the aromatic acetylene hydrocarbon-phenyl acetylene (PhA) by the Favorsky method, AAC may be obtained synthesizing.

Available aromatic acetylene alcohols (AAA) - 2-methyl-4-phenylbut-3-yn-2-ol (I), 3-methyl-1-phenylpent-1-yn-3-ol (II), 3,4-dimethyl-1-phenylpent-1-yn-3-ol (III), 3,4,4-trimethyl-1-phenylpent-1-yn-3-ol (IV), 2,4-diphenylbut-3-yn-2-ol (V) and 1-phenylhex-4-en-1-yn-3-ol (VI) is synthesized by the influence of acetone, methyl ethyl ketone, methyl propyl ketone, pinokaline, acetophenon, croton aldehyde on link- and tribond-bearing phenylacetylene. Synthesis reaction scheme of AAA is offered in the following view on the references.

\[
\begin{align*}
\text{Ar} & + \text{R} \xrightarrow{\text{MOH+solvent}} \text{R'} \\
\text{Ar} & \text{C} \xrightarrow{\text{OH}} \text{R}
\end{align*}
\]

Here: R = -CH₃, R¹ = -CH₃; R = -CH₃, R¹ = -C₂H₅; R = -CH₃, R¹ = -C₃H₇; R = -CH₃, R¹ = -C₆H₃, R = -H, R¹ = -CH=CH-CH₂-M = Li, Na and K, solvent- methanol, methanol, DEE and TGF.

Anticorrosion properties of AAA, synthesized on the basis of phenyl acetylene, anti (erosion) decay of metal and metal installation under the affect of alive microorganisms, including bacterium and funguses occurring in the content of oil have been studied. Biocorrosion is also called bacteriological or fungous corrosion. It is cleared that 30 % of biocorrosion of metals is caused by microfunguses, 70% by microbacteria. These microorganisms call metal biocorrosion into being and it is observed that it creates opportunity for the growth of chemical corrosion.

As a result of microbiological corrosion of metal pipes and apparatus oil industry is suffering losses in general manufacture for 5-10%. Alongside with being cause of corrosion of installation, microorganisms are reasons for the damage of oil composition - hydrogen sulphide corrosion. Studying the reasons of biological corrosion and their occurrence, and creating chemical preparations preventing corrosion are considered one of important tasks in front of science.

Inhibitor properties of synthesized AAA anti bacterium and funguses causing the decay of metal installation in oil fields by the influence of microorganisms have been studied. Kinds of microorganisms-bacterium and funguses originating the process of biocorrosion in the metal installation, machines, tools of drilling, storage, delivery, and also in the refinery have been determined. As the object of investigation Kukbulok, Umid, Kruk and Northern Urtabulak in the system of "Uzbekneftegaz" NHC have been chosen. As a result of investigations more than 100 hydrocarbon oxidizing bacteria sludge (slime) have been isolated from filings removed from water-oil emulsions, pipes and machines. It has been defined that more than 40 of them affect the quality of oil and oil products and metal installation biocorrosion.

Results of investigation show that it has been defined the influence of sulfate -reducing bacteria removed from AAA samples on the stimulants of biocorrosion of oil industry pipes.

It has been defined that among the suggested biocides microorganisms in the composition of V and I oil and oil products are the most active biocide anti funguses and bacteria.
Section 3

Chemistry and Technology of Medical Products and Biologically Active Compounds
The steroid nature hormones represent polycyclic compounds of lipid nature, which structure basis is a-cyclic hydrocarbon of cyclopentanoperhydrophenanthrene, consisting of three 6-membered and one 5-membered hydrocarbon rings. Sterane core causes polymorphous unity of the structure and functions of a class of steroid hormones. The discrepancy of their properties is determined by the combination of relatively small modifications in the structure of the skeleton. Chemical structure of glucocorticoids belongs to the C21-steroids with pregnane skeleton.

Corticosteroids, among them the most widely used in medical practice is hydrocortisone, are known as hormones, lowering inflammation by reducing inflammatory cell infiltration and migration of leukocytes and lymphocytes into the area of inflammation. The other side of the effect of introduced into the body hydrocortisone, associated with its influence on the embryogenesis and implementation of reproductive function in animals and humans is poorly studied.

In this regard, the aim of the work was to investigate the effects of exogenously administered particular steroid hormone hydrocortisone on the dynamics of spawning, the course of embryogenesis and some features of post-embryonic development of the pond snail *Lymnaea stagnalis*, which was used as a model object.

The effect of a standard solution of hydrocortisone (Sigma - Aldrich, USA) and medical drugs was studied. The drugs were administered by intramuscular injection into the fabric legs. Working concentration and dosage of the hormone corresponded to physiological ones.

In the result, it was found that the standard of hydrocortisone reduced the range of the timing of spawning, changed the nature of spawning activity. It was observed that there was a reduction of fecundity of molluscs, accompanied by a pronounced increase in the size of masonry that is probably connected with the stimulation of the accessory glands of the hormone.

The period of embryogenesis in injected shellfish completed 10 hours earlier than in the control group. The maximum degree of the stimulating effect of hydrocortisone emerged on stage gastrula and veliconcha. A very similar passage of certain stages of embryonic development of *Lymnaea stagnalis* stimulating effect was observed in medication hydrocortisone. The difference obtained when comparing the results totaled 5 hours.

At the stage of postembryogenesis hydrocortisone reduced hatching time of juveniles and changed the dynamics of this process. Hormone significantly inhibited the growth processes, and its effect was intensified in the course of time.

Thus, it can be assumed that the hit hormone leads to disruption of the hormonal homeostasis, and as a result, disturbance of the normal embryonic development, implementation, reduce the period of spawning, reduced fertility and reproductive activity of the object model and inhibition of growth processes initially postembryogenesis.

Thus, we can assume that hormone entry leads to the hormonal homeostasis disruption, and, as a consequence, to normal embryonic development disorder, spawning time reduction, fecundity decrease and drop in reproductive activity of the model object, as well as the inhibition of growth processes at the initial stage of postembryogenesis.
FEATURES STUDY OF ONE OF THE METHODS OF VEGETABLE RAW MATERIALS DEEP PROCESSING WITH THE AIM OF CREATION OF PRODUCTION TECHNOLOGY OF IMPORT-REPLACING BIOLOGICALLY ACTIVE SUBSTANCES

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Lately there is a trend towards the increase of scientific development of technological bases of obtaining of various chemicals (industrial chemicals) for the production of biologically active substances on the basis of non-crude oil derived raw materials but with the use of traditional methods and techniques of deep processing of products which are vegetable by nature. This is because the use of them or their derivatives helps to find a reasonable solution to the problems arising with the manufacturing of widely used products, such as: elastomers, plastisol, adhesive compositions, plastics and other household products, which necessarily must be non-toxic and biodegradable.

The present work is devoted to the development of simple and available methods of deep processing of vegetable raw materials with the aim of creating the technology of import-replacing production of biologically active substances (e.g. biodegradable surfactants and other chemical products). Similar compounds, based on raw materials of plant (vegetable) and animal origin, are known since the late 19th century and they are still widely used in the manufacturing of soaps, rubber goods and tyre production industries. However, significantly intensive development of chemistry in this area occurs lately. This relates to identifying interesting areas of their application, as basic components in the course of deep processing of plant raw material and as intermediate products. For example, in the form of their esters (which are different in properties rather than the original samples of vegetable oils), severe shortage of which was discovered after the imposition of economic sanctions against Russia.

In the work, to be presented at the conference, simple and affordable methods to produce a number of biologically active substances will be reviewed. In the overseas countries the production of such a substances is established on the basis of missing in Russian Federation exotic types of vegetable oils and animal fats. As import substitution for the production of the same biologically active substances, it is proposed to use domestic wood processing products – tall oil and its derivatives (complex esters of aliphatic alcohols and fat non-saturated C18 acids or their derivatives).

Interest to the synthesis of such chemicals is largely due to the fact that they can be easily obtained by esterification of lower aliphatic alcohols (methyl, ethyl, propyl, butyl, etc.) by fatty acids, of e.g. tall oil or by the alcoholysis of various samples of industrial vegetable oils in the presence of acid or alkaline catalysts. These processes occur under mild conditions with the use of available process equipment (a vessel with a stirrer or continuous reactor – it is preferable to use a vessel, that is close to plug-flow reactor).

Demo plant testing of the developed process showed its promising use in various areas of industry, especially because the chemistry and technology of processing of such natural renewable hydrocarbon sources is the basis of "green" chemistry and in the future it will probably occupy one of leading places in the chemical industry in the area of production and modification of bioplastics or in the area of synthesis of the individual components for their further production.
CASCADE TRANSFORMATIONS INITIATED BY ELECTRON TRANSFER IN THE SYSTEM OF DONOR-ACCEPTOR

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Modern organic synthesis of pharmaceuticals and other biologically active substances requires high efficiency: minimizing the number of steps of the process while increasing the complexity of taking place transformations. During cascade reactions there are formation of a several chemical bonds in a single reactor without addition of reagents or conditions change. This increases the overall yield of the multistage process, thereby reducing production costs.

An example of cascade reactions, we have studied, is a reductive cyclization of N-(2-nitro(het)arylp)pyridinium salt, allowing to obtain polycyclic condensed imidazole derivatives having a bridgehead nitrogen atom with high biological activity. This process begins with the transfer of electrons and protons to the contained in the substrate nitro group and converting it into an active nucleophilic species - hydroxylaminogroup. Last attacks α-carbon atom of the pyridine ring with the formation of C-N bond:

\[ \text{N}^+X^+ + 4e^- + 4H^+ \rightarrow \text{N}^+X^+ + 4H_2O \]

This method has allowed to obtain in mild conditions (T = 30-40 °C, 2% HCl: i-PrOH = 1: 1, 1-10 min) a series of tricyclic condensed imidazole derivatives having a bridgehead nitrogen atom with high yields (71- 98%). With the help of DFT calculations the mechanism of the reaction was revealed. Structure of some compounds was determined by X-ray crystallography. The characterization of all novel synthesized heterocycles was done by \(^1H\), \(^13C\) NMR, MS, and HRMS. Simplicity and soft execution of our synthetic procedure are the main advantages leading to the creation of an important library of condensed imidazole derivatives, bearing different electron withdrawing groups. It is planned to extend the tandem transformation methodology for the synthesis of other nitrogen-containing tri-, tetra- and pentacyclic systems for the production of pharmacologically active substances.

**Acknowledgements:** The work was supported by the Russian President's scholarship for young scientists and graduate students engaged in advanced research and development in priority areas of modernization of the Russian economy in the 2016-2018 years. Order of the Ministry of Education of Russia on April 5, 2016 № 375.
SYNTHESIS AND FUNCTIONALIZATION OF CONDENSED PYRAZINE DERIVATIVES

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Fused pyrazine derivatives have many areas of application. They possess a variety of pharmacological activities: antibacterial, antifungal, antitumor, malaria and antitubercular. Pyrazine ring is a part of different antibiotics. For example, Brimonidine is a drug for glaucoma’s treatment. Pyrazinamide is used in the initial stages of tuberculosis. In this regard, obtaining new pyrazines is an actual problem of modern organic chemistry. Therefore, different ways of synthesis of novel fused pyrazine derivatives have been developed in this paper.

Optimization of the reaction conditions used for the synthesis and functionalization of fused pyrazine and pyrazinone derivatives allowed synthesizing a few new heterocyclic products. The structure of all compounds was established using the complex of physico-chemical methods of analysis: NMR and IR spectroscopy and high resolution mass spectrometry.

Acknowledgements: The work was supported by the Russian President's scholarship for young scientists and graduate students engaged in advanced research and development in priority areas of modernization of the Russian economy in the 2016-2018 years. Order of the Ministry of Education of Russia on April 5, 2016 № 375.
The study of intermolecular interactions between biologically-active substances - ribavirin and interferon-alpha-2b is of particular interest because the mechanism of their joint action against the hepatitis C virus is not clear yet.

In aqueous solutions ribavirin molecule shows surface activity (Fig. 1). Table 1 illustrates the parameters of adsorption layers - surface activity (g), the value of adsorption ($\Gamma_{\text{max}}$), the landing area ($S_0$) and the layer thickness ($\delta$).

Table 1. Parameters of adsorption layers of ribavirin

<table>
<thead>
<tr>
<th>g, mJ-m/mol</th>
<th>$\Gamma_{\text{max}}$, $\mu$mol/m^2</th>
<th>$S_0$, nm^2</th>
<th>$\delta$, nm^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>on the interphase boundary between water solution and air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,25</td>
<td>1,38</td>
<td>1,20</td>
<td>0,16</td>
</tr>
<tr>
<td>on the interphase boundary between water and decane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,50</td>
<td>1,52</td>
<td>1,15</td>
<td>0,15</td>
</tr>
</tbody>
</table>

In the mixed aqueous solutions there occur intermolecular interactions between protein molecules and ribavirin, affecting the critical constants association. Intermolecular interactions between protein molecules and ribavirin, which affect the critical constants association, occur in the mixed aqueous solutions. With the presence of ribavirin the CCA of interferon is significantly lower (Fig. 2, Table 2).

Table 2. Associations characteristics of interferon

<table>
<thead>
<tr>
<th>Ratio &quot;Interferon-ribavirin&quot;</th>
<th>CCA, g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure interferon</td>
<td>0,25</td>
</tr>
<tr>
<td>Pure ribavirin</td>
<td>16,95</td>
</tr>
<tr>
<td>1:1</td>
<td>0,16</td>
</tr>
<tr>
<td>1:2</td>
<td>0,13</td>
</tr>
<tr>
<td>1:5</td>
<td>0,02</td>
</tr>
</tbody>
</table>

Reference:
SYNTHESIS AND STUDY OF SPECIFIC ACTIVITY IN VITRO OF $^{177}$Lu LABELED (scFv/4D5-HSA-DOTA-) COMPLEX TARGETING HER2/NEU-POSITIVE BREAST CANCER CELLS

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Tumor-targeting radionuclide delivery aimed to enhance the efficacy and safety of the radionuclide application for anti-cancer treatment is a promising area of biomedical research and nuclear medicine. The human growth factor receptor type 2 (HER2/neu) is overexpressed in certain aggressive types of breast cancer and could be considered as a reasonable target for such approach.

In this study a radioimmunoconjugate consisting of recombinant scFv fragments of a humanized anti-HER2/neu 4D5 antibody conjugated with human serum albumin (HSA) and labeled with $\beta$-emitting $^{177}$Lu radionuclide via DOTA-NSH-ester chelator was synthesized and evaluated in vitro.

The technology developed for scFv/4D5-HSA-DOTA-$^{177}$Lu synthesis provides a high decay-corrected radiochemical yield of the conjugate (more than 85%). The stability of the synthesized $^{177}$Lu-labeled conjugate in physiological solutions (saline, human blood serum) during at least 10 days was shown.

HER2/neu-overexpressive breast cancer cells (BT-474 cell line) and breast cancer cells having low-level HER2/neu expression (MCF-7 cell line) were used for the comparative study of the antigen-specific uptake and the cytotoxicity of the $^{177}$Lu-labeled complex. The overexpression of HER2/neu on BT-474 cells was confirmed by immunocytochemistry. The immunoreactivity of the scFv/4D5 was demonstrated on BT-474 cells using flow cytometry by competition receptor-binding assay. The cytostatic effect of the scFv/4D5 on the BT-474 cells was found to be identical to trastuzumab. Accumulation of scFv/4D5-HSA-DOTA-$^{177}$Lu in cells was performed in a serum-supplemented medium and was estimated by measuring of residual $^{177}$Lu activity in cell lysates by $\gamma$-spectrometer. The surviving fraction of BT-474 or MCF-7 cells treated with scFv/4D5-HSA-DOTA-$^{177}$Lu in vitro was determined by MTT-assay.

The results of the uptake study showed that $^{177}$Lu activity in BT-474 cell lysates measured after 24 h and 48 h of incubation in 3-5 times exceeds the radioisotope activity in MCF-7 cell lysates.

After 5-days exposure with scFv/4D5-HSA-DOTA-$^{177}$Lu (10\textsuperscript{6} Bq of $^{177}$Lu activity) a significant decrease of the BT-474 cells viability was observed.
DIMENSIONAL CHARACTERISTICS OF NANOCOMPOSITES OF DAUNOMYCIN WITH POLYVINYLPYRROLIDONE AND SELENIUM NANOPARTICLES

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Search strategy of new antitumor agents based on conjugates of anthracycline antibiotics and macromolecules and (or) nanoparticles of bioactive elements is of current interest of modern research in the field of medicinal chemistry.

Objective of the work is the development of methods of synthesis of nanocomposites of selenium (Se) nanoparticles, bioactive polymer polyvinylpyrrolidone (PVP) and anthracycline antitumor antibiotic daunomycin (DM), as well as a study of obtained nanocomposites using the dynamic light scattering in order to create an anticancer drug with high selectivity and low toxicity. Two possible methods of synthesis of nanocomposites were investigated. In the method I selenium nanoparticles were pre-stabilized with PVP in the process of reaction (1) and then DM was added. Method II was implemented by obtaining a preliminary complex between DM and PVP, followed by the reaction (1) of synthesis of nanoparticles.

\[
\text{H}_2\text{SeO}_3 + 2\text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{Se}^+\text{3H}_2\text{O} + 2\text{C}_6\text{H}_6\text{O}_6
\]  

The figure shows the \( C_{\text{Se}} \) concentration dependence of structural and conformational parameter \( \rho = R_g/R_h \), where \( R_g \) is hydrodynamic radius, and \( R_h \) is the mean square radius of inertia. The dimensional characteristics of nanocomposites synthesized by the method I differ greatly from that of the PVP-Se nanocomposite and nanocomposites obtained by the method I as solid spherical formations with a rather homogeneous structure. This may be due to the relatively dense laying of long PVP molecules on the surface of the Se nanoparticles, and injection of DM after the formation of the double nanocomposite does not lead to significant changes in the structure. In the case of method II the value of \( \rho \) changed in a wider range (1 ÷ 0.74). Probably, in this case the Se nanoparticles are «embedded" into the formed PVP-DM complex arbitrary manner, which leads to less dense formations. Therefore, increasing the amount of Se nanoparticles in the nanocomposite affects its structural organization, which makes it possible to adjust its dimensional characteristics. Information about the correlation between structural organization of the nanocomposite and its dimensional characteristics will allow in prospect to affect the pharmacokinetics of antitumor antibiotic.
The work is devoted to a multistep synthesis of chlorins derivatives conjugates with cyclic polyamine for further creation of theranostic agent by the introduction of gadolinium cation.

Currently a lot of interest in the chemistry of biologically active compounds is attended to synthetic derivatives of chlorins and their conjugates. The nucleophilic addition to 13\textsuperscript{1}-st oxogroup proceeds selectively (Scheme).

The 1,4,7,10-tetraazacyclododecane (cyclen) was selected as the cyclic polyamine initial substance. Nitrogen atoms nucleophilic properties in cyclen are enough to open exogenous pentanone ring in pheophorbide \(a\).

The next step was the alkylation of nitrogen atoms in cyclen by tert-butyl ester of \(\alpha\)-monobromoacetic acid. Reaction controlling was carried out by thin layer chromatography (TLC) because triester Rf value increased significantly. Introduction of three acetic acid residues in the molecule of the conjugate was confirmed by mass and NMR spectra. Deblocking of the tert-butyl groups by 80\% TFA acidolysis yielded precursors, which can chelate cations of different transition metals.

Synthesis of gadolinium containing conjugate precursor.

The substituted cyclen chlorins conjugates can bind several different cations to one molecule in order to obtain heteronuclear conjugates. On this basis highly effective photosensitizers and fluorescent label contrast agents used in medicine for multimodal diagnostics can be established. Their potential applications are photodynamic therapy (PDT), magnetic resonance imaging (MRI) or positron emission tomography (PET).

**Acknowledgements**

The work was supported by RFBR research project No. 15-03-02988 and grant of President of Russian Federation for state support of leading scientific schools of the Russian Federation НШ-7946.2016.11.
PROCEDURE OF PREDICTING AN ANTITUMOR EFFECT OF TARGETED IMMUNOTHERAPY DRUGS

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Prediction antitumor effect of targeted drugs immunotherapy, connected with analysis of the effect changes levels of transcription specific cytokines on change in proliferative activity of cancer cells.

The data on the levels of cytokine transcription and biological activity cells of lung carcinoma were obtained in Gamaleya Federal Research Center of Epidemiology and Microbiology of the Ministry of Health of the Russian Federation.

Mechanism and the reasons for change cell functional activity, has been defined through the study of cytokine production on the level of transcription in vitro in cell cultures after incubating the cells with drugs.

Changes level of transcription cytokines evaluated qualitatively (either exists or not). Change proliferative activity of cancer cells of lung carcinoma also assessed qualitatively (whether there is a change compared with the control sample).

Contingency tables, applied for statistical univariate analysis, can be used to account for joint effect selected factors. For such a multivariate analysis, was using the procedure inhomogeneous sequential procedure. This procedure is based on the method of sequential statistical analysis of Wald and allows to build a predictive scale scores by calculating the specific prognostic factors and evaluation of their information.

Based on use of inductive inference methods proposed a model of predicting proliferative activity of cancer cells, based on the relationship hypothesis of cytokines combination. The methodology takes into account the synergies of cytokines and uses the sequential construction of logical formulas for selecting groups of cytokines, statistical analysis of contingency tables and construction of prognostic scales. Implementation of the proposed method according to the informational prediction system antitumor effect of targeted therapies immunotherapy, will significantly accelerate research in this area.
Herbal medicine in recent years, becoming an important component in the treatment of urolithiasis (IBC). In this disease the use of herbal remedies most efficiently in cases of long reception of medicines for the effective maintenance of intensive treatment, reduce side effects of chemotherapy, improve the efficiency of complex treatment. It is obvious that in chronic inflammatory diseases of the genitourinary system of herbal medicine greatly expands the possibilities of medicine, where prolonged exposure to conventional chemotherapeutic agents are insufficiently effective or are contraindicated. At present, a few tens of medicinal herbs, usually in the form of fees, used to treat IBC. The advantage over synthetic drugs charges lies in the substantial absence of complications and undesirable side effects; increases the choice of exchange rate application circuits, eliminating the addictive, reducing the final result; expanding the possibility of selection of combinations of medicinal herbs, which, on the one hand reinforce the properties and on the other - to provide a flow of the patient all the necessary set of biologically active substances (flavonoids, essential oils, polyphenols, etc.). ICD - a complex physical-chemical process that is associated with impaired kolloidal balance in the body. Currently available domestic and foreign drugs are not highly effective for litholysis, especially calcium oxalate stones. Therefore, the development of new herbal remedies or herbal remedies complex with known drugs and to study their properties litoliznyh is an extremely important task, as it can exclude from surgery or other traumatic methods of treatment of urological patients. The aim of the work was to develop and study litholytic activity of new herbal remedies on the basis of charges of different herbs, which are intended for the effective treatment and prevention of various types of nephrolithiasis (oxalate, phosphate, urate) .. To create herbal remedies used various combinations of herbs. Optimal gathering of plants that achieve effective litholysis at nephrolithiasis. This research enables us to conclude grounds that the action of herbal extracts become more effective when applied in two stages, the composition of charges on the first and second phases differ from each other. This therapeutic approach provides a gentle on the concretions and does not cause undesirable side effects in patients.
USING COPOLYMER OF METHYL METHACRYLATE AND METHACRYLIC ACID IN ASSOCIATION WITH WATER-SOLUBLE POLYMERS FOR MICROENCAPSULATION OF BIOLOGICALLY ACTIVE SUBSTANCES

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Short presence of many drugs in the body is one of the major challenges of modern pharmacology. This explains the impossibility to create in the blood and tissues of uniform therapeutic concentration of the active substance for a long time. Therefore, one of the main ways to improve the effectiveness of pharmacotherapy is a creation of formulations with sustained release of active substance by microencapsulation techniques.

The purpose of this study is to investigate the features of microencapsulation process poorly water-soluble drugs. As an example of a drug we used furatsilin which was encapsulated in a single or double shell from copolymers of methacrylic acid and methyl methacrylate, and polyvinyl alcohol (PVA) or polyvinylpyrrolidone (PVP).

As the material forming the inner shell of the microcapsules were selected methacrylic acid derivatives under the trade name «Eudragit®». This polymer being water-insoluble and biodegradable, designed to provide sustained release of the drug in a particular area of the human body. Imparting of this composition ability to dissolve in water will simplify the use of the resulting product and increase its bioavailability.

Encapsulation furatsilina in Eudragit® L100 was carried out by physico-chemical method. The process carried on a magnetic stirrer at room temperature. To the aqueous dispersion of furatsilina was added dropwise polymer solution in dichloromethane or acetone. Then to a water-acetone dispersion of capsules furatsilina in Eudragit® dropwise added an aqueous solution of a second polymer (PVA or PVP) and then acetone or ethanol to achieve complete precipitation of the water-soluble polymer. The resulting product was isolated by filtration or centrifugation and dried in air.

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.

Encased into the shell from copolymers of methyl methacrylate and methacrylic acid furatsilin acquires the ability to prolonged release in the body thereby creating a uniform therapeutic concentration of the drug in tissues and organs. In case if as the second shell apply water soluble polymer (PVP or PVA), then such product can form stable aqueous dispersions. Herewith prolonged effect of the obtained preparation is fully preserved.

So, the use of single or double shells for microencapsulation of drugs would solve one of the pharmacology problems consisting in the rapid removal of the drug from the body. Imparting to the resulting composition the ability to form stable aqueous dispersions makes it possible to create different types of finished dosage forms.

References:
PHOTOCHEMICAL PROPERTIES OF DOUBLE-DECKER PHTHALOCYANINE COMPLEXES OF YTTERBIUM AND LUTETIUM

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It is known that K3 vitamin participates in tissue respiration – recovery reactions, such as transfer of electrons and also possesses antihemorrhagic activity. However its activity decreases at radiation or freezing. In this connection, it is necessary to develop ways of activation of vitamin K3.

Double-decker lanthanide phthalocyanine complexes find broad application in various field of science and equipment. The main feature of phthalocyanine complexes Lu and Yb is their ability to pass of an electron between two stable forms (radical [Pc2–MIII–Pc2–]0 and anion [Pc2–MIII–Pc2–]). Influence of the environment on transition between two stable forms in polymers, micelles and proteins was detailed studied [1, 2].

In this work photochemical activity of LnPc2 (Ln = Yb, Lu) in process of transfer of an electron has been established. In process radiation (λph = 620 nm) double-decker lanthanide phthalocyanine complexes passes from the anion form into the radical form. At the same time there is a restoration 2-methyl-1,4-naphthoquinone (analogue of K3 vitamin).

![Diagram of electron transition]

Acknowledgements
This work was supported by RFBR (project № 15-03-03591).

References:
ALTERATIONS IN THE COMPOSITION OF LIPIDS AND FATTY ACIDS IN FUNGI UNDER THE INFLUENCE OF EXTERNAL FACTORS

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The heat shock (HS) response is an adaptation of organisms to elevated temperature. It includes substantial changes in the composition of cellular membranes, proteins and soluble carbohydrates. To protect the cellular macromolecules, thermophilic organisms have evolved mechanisms of persistent thermotolerance. Many of those mechanisms are common for thermotolerance and the HS response. However, it remains unknown whether thermophilic species respond to HS by further elevating concentrations of protective components. We investigated the composition of the soluble cytosol carbohydrates and membrane lipids of the thermophilic fungi *Rhizomucor tauricus* and *Myceliophthora thermophila* at optimum temperature conditions (41–43 °C), and under HS (51–53 °C). At optimum temperatures, the membrane lipid composition was characterized by a high proportion of phosphatidic acids (PA) (20–35 % of the total), which were the main components of the membrane lipids, together with phosphatidylcholines (PC), phosphatidylethanolamines (PE) and sterols (St). In response to HS, the proportion of PA and St increased, and the amount of PC and PE decreased. No decrease in the degree of fatty acid desaturation in the major phospholipids under HS was detected. The mycelium of all fungi at optimum temperatures contained high levels of trehalose (8–10 %, w/w; 60–95 % of the total carbohydrates), which is a hallmark of thermophilia. In contrast to mesophilic fungi, heat exposure decreased the trehalose level and the fungi did not acquire thermotolerance to lethal HS, indicating that trehalose plays a key role in this process. This pattern of changes appears to be conserved in the studied filamentous thermophilic fungi. The second task was to study the regulatory effect of exogenic omega-hydroxyderivatives of linoleic and linolenic fatty acids on the sexual and asexual sporulation of fungi *Neurospora crassa* (wild-type strain and mutants on proteins of photoreceptor complex). In wild type strain hydroxyderivative of linoleic acid, unlike hydroxyderivative of linolenic acid, stimulated protoperithecia formation in the dark and in the light. In the same strain the studied oxyderivatives influenced formation of conidia only under illumination. Hydroxyderivative of linoleic acid stimulated and hydroxyderivative of linolenic acid inhibited the conidia formation. Oxyderivatives of fatty acids had no effect on protoperithecia formation in photoreceptor complex mutants, which apparently indicated its involvement in signal transduction in *Neurospora crassa*.

Acknowledgements
The work was partially supported by the Russian Ministry of Education and Science, State task, project No. 4.128.2014/K.
UDC 577.1

**CHLORIN \( e_6 \) BASED IR PHOTOSENSITIZERS FOR PHOTODYNAMIC AND ANTIMICROBIAL THERAPY**

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Photosensitizers (PS) became popular drugs in the last decades. It can be explained by simplicity and noninvasive characteristics of the process of PDT (photodynamic therapy). PDT is a promising new treatment modality for several diseases, especially cancer. In PDT, light, \( O_2 \), and a photosensitizing drug are combined to produce a selective therapeutic effect. The antimicrobial therapy is provided in the same manner. The PS in this case should be positively charged because the membrane of bacteria is charged negatively. Studies are underway to create new photosensitizer candidates, because the most commonly used porphyrin photosensitizers are far from ideal with respect to PDT and antimicrobial therapy. Finding a suitable photosensitizer is crucial in improving the efficiency of PDT. Chlorins seem to be promising candidates for 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 50-75%. In case of preparation of cationic PS we performed reaction of methylation of the compounds obtained \( 2a,b \) by adding excess of methyl iodide in chloroform at room temperature.

The purity and the structure of all the compounds obtained were confirmed by methods of TLC, electronic, IR, \( ^1H \)-NMR spectroscopy and mass-spectrometry.

The work was financially supported by the Russian Foundation for Basic Research (project № 16-33-00856-mol_a) and grant of President of Russian Federation for state support of leading scientific schools of the Russian Federation HIII-7946.2016.11.
Since its discovery 8-oxo-2'-deoxyguanosine (8-oxo-dG) began to be used as a biomarker of oxidative DNA damage and diseases associated with them, as well as aging. For a long time it was customary to consider this compound as a by-product of oxidative metabolism having no important functions in the body. Furthermore, 8-oxo-dG was considered as a potential mutagen, although it was shown soon enough that it is almost not included in the cellular DNA when it is added from the outside.

However, in recent years there have been publications showing a significant bioregulatory role and even potential pharmaceutical significance of 8-oxo-dG. Korean researchers demonstrated by experiments in mice a wide range of immunomodulating and anti-inflammatory activity of exogenous 8-oxo-dG in high doses. The therapeutic effect of this compound has been shown in models of asthma, type II diabetes, sepsis, autoimmune encephalomyelitis, ovalbumin allergy and atherosclerosis.

At the same time, several groups of researchers have shown a pronounced protective role of 8-oxo-dG in cell cultures growing under adverse conditions, including fasting, irradiation and hypoxia. External use of 8-oxo-dG could also protect against UV damage to the skin of mice sensitive to radiation.

We can assume that all this is based on a common mechanism of activation of general stress response of organisms that includes limiting its own production of ROS as a result of immune responses, as well as activation of repair systems, antioxidant defense and stress. Our experimental data confirm this assumption. These data show a protective effect of 8-oxo-dG in models of heat shock and steady aging of the cell culture.

In this case, 8-oxo-dG is a potential new class of drug that can be useful in the treatment of autoimmune and inflammatory diseases and as a preventive protection means at high risk of oxidative damage of biomolecules. For example, a compound with a similar effect could be applied as a means of protection in the preoperative period to accelerate the subsequent recovery or for people who have to work with radiation, X-ray or ultraviolet light.

The proposed technologies for quantifying 8-oxo-dG in DNA make it possible to use it for a variety of diagnostic applications, and development of new lower-cost approaches to its synthesis will give the opportunity to explore in detail its biological function.
MODIFIED POLYMER-CONTAINING CATALYSTS FOR SELECTIVE HYDROGENATION 2-METHYL-3-BUTYN-2-OL – INTERMEDIATE PRODUCT IN SYNTHESIS OF FRAGRANCE COMPOUNDS AND FAT-SOLUBLE VITAMINS

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Selective hydrogenation of acetylene alcohols is widely used in fine organic synthesis, especially in production of fragrances, biologically active compounds and fat-soluble vitamins A, E and K [1]. Palladium is well known to be the most selective catalyst for hydrogenation of triple -C≡C- bond of alkynols. However, the achievement of high selectivity along with reasonable activity is the main issue concerning industrial hydrogenation of alkynols. One of the approaches allowing increasing the affectivity of hydrogenation catalysts is the introduction of second metal-modifier. Commercial Lindlar catalyst (Pd/CaCO₃) containing lead acetate and quinolone was the first example of modified palladium catalyst for selective hydrogenation [3]. However, the use of these modifiers leads to pollution of the target products and environmentally unfavorable.

The introduction of first group metal cations (e.g. Na⁺, K⁺) is an alternative method to increase activity and selectivity of catalytic systems. Cho H.-B. et al. [2] have shown that the most effective Pd-containing hydrogenation catalysts can be synthesized while using post-impregnation modification method.

In the framework of this work, Pd immobilized in polymeric matrix of hypercrosslinked polystyrene (HPS) of MN100 type bearing amino-groups was used for the synthesis of modified catalysts (Pd content was 0.7% (wt.) according to elemental analysis). The series of modified catalysts was synthesized via post-impregnation method at variation of alkali metal precursor nature (NaOH, KOH, K₂CO₃, Na₂CO₃, KH₂PO₄, NaH₂PO₄).

All the synthesized samples were tested in the reaction of selective hydrogenation of 2-methyl-3-butyn-2-ol – the intermediate product in the synthesis of fragrant compounds (such as linalool, linalyl acetate, citral, citronellol etc.) and vitamins A, E and K. Catalytic testing was carried out in a 60 mL isothermal glass batch reactor installed in a shaker and connected to a gasometrical burette (for hydrogen consumption control). The total volume of liquid phase was 30 mL. Toluene was used as solvent. Temperature of reaction was 90°C. Samples were analyzed via GC-MS (Shimadzu GCMS-QP010S).

The variation of alkali metal precursor nature was shown to has strong influence on the catalytic behavior. Modified catalysts showed higher activity and selectivity in comparison with the unmodified freshly prepared sample. The highest selectivity (99% at 95% of substrate conversion) was achieved for 0.7%-Pd/MN100 catalyst modified with KOH, whereas the unmodified catalyst showed 97.5% selectivity at 95% of substrate conversion. For comparison, the use of commercial Lindlar catalyst (2%-Pd/CaCO₃) allows achieving 95% selectivity at 100% of substrate conversion [4].

Acknowledgements
The study was funded by the Russian Science Foundation, the project 15-19-20023.

References:
SORBTION OF THREONYLTHREONINE DIPEPTIDE AND THREONINE FROM THEIR MIXTURES

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The pharmacological activity of the peptides determines their relevance as active ingredients for the production of medicaments. The basic method for their preparation is directed peptide synthesis, the final product can contain the impurities of the starting components - amino acids. Using dipeptides as pharmaceutical substances involves their deep cleaning from the concomitant components. Effective cleaning methods for peptides and amino acids are sorbtion methods. In the present study we investigated the possibility of separation of the dipeptide threonylthreonine (Thr-Thr) with cytoprotective properties, and its concomitant amino acid threonine (Thr) using anion exchanger AB-17 (OH-).

We studied the sorbtion of Thr and Thr-Thr from individual solutions and their mixtures with different concentrations and molar ratio of the components. The table lists the values of distribution coefficients of Thr (D_A) and Thr-Thr (D_P) from mixtures and individual solutions in the same equilibrium concentration in the aqueous phase C_p (mmole/l), and the separation coefficients calculated by the formula: β=D_P/D_A when the sorbtion is from mixture – β_e, and separation coefficients theoretically calculated using the distribution coefficients Thr and Thr-Thr from individual solutions – β_t.

<table>
<thead>
<tr>
<th>Thr/Thr-Thr, mole/mole</th>
<th>From two-component mixtures</th>
<th>From individual solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_p(A) mmole/l</td>
<td>C_p(P) mmole/l</td>
</tr>
<tr>
<td>1/1.197</td>
<td>7.23</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>10.17</td>
<td>6.04</td>
</tr>
<tr>
<td></td>
<td>14.45</td>
<td>12.94</td>
</tr>
<tr>
<td></td>
<td>28.99</td>
<td>28.66</td>
</tr>
<tr>
<td>1/4.688</td>
<td>2.48</td>
<td>5.31</td>
</tr>
<tr>
<td></td>
<td>3.47</td>
<td>9.76</td>
</tr>
<tr>
<td></td>
<td>4.96</td>
<td>15.99</td>
</tr>
<tr>
<td></td>
<td>9.92</td>
<td>37.56</td>
</tr>
<tr>
<td>1/10.63</td>
<td>1.20</td>
<td>6.54</td>
</tr>
<tr>
<td></td>
<td>1.68</td>
<td>10.58</td>
</tr>
<tr>
<td></td>
<td>2.40</td>
<td>17.44</td>
</tr>
<tr>
<td></td>
<td>4.79</td>
<td>39.06</td>
</tr>
</tbody>
</table>

In case of sorbtion from the mixture, the distribution coefficients of the amino acid are reduced with reducing of its molar ratio in the solution and remain virtually constant with increasing C_p. D_A values obtained during sorbtion from mixtures are considerably lower than those of the individual solutions. On the contrary, D_P from mixtures and from solutions have similar values at identical C_p. D_P is practically independent of the molar ratio Thr/Thr-Thr in the mixture, indicating a slight influence on the selectivity of the anion exchanger AB-17 to the dipeptide is present in the solution of threonine. The findings indicate that the use of the anion exchanger AB-17 (OH-) is promising for the separation of Thr-Thr and Thr mixtures.
Interest in the conjugates of tetrapyrole compounds and fullerenes is connected with their unique photophysical properties and the ability to create new organic photoconductive materials, nanomaterials and biologically active compounds of a wide spectrum of action. We have developed approaches to the synthesis of chlorin-fullerenes with various positions of fullerene fragment in the chlorin macrocycle using the 1,3-dipolar cycloaddition of nitrile oxide produced from the hydroxyiminomethyl-substituted chlorin in the presence of (diacetoxyiodo)benzene, to the double bond of the fullerene under mild conditions. The starting chlorophyll \( \alpha \) derivatives purpurin 18 and chlorin \( p_6 \) 13,15-\( N \)-hydroxycycloimide were condensed with 4-carboxybenzaldehyde or 4-hydroxybenzaldehyde in the presence of EEDQ to form the corresponding formyl-containing chlorins which were converted into oximes by the reaction with hydroxylamine hydrochloride in pyridine. 3-Hydroxyiminomethyl derivative of chlorin \( p_6 \) \( N \)-methoxycycloimide was synthesized by successive oxidation of the vinyl group of \( N \)-methoxycycloimide with sodium periodate in the presence of osmium tetroxide and the treatment of 3-formylchlorin obtained with hydroxylamine. The resulting oxime reacted with (diacetoxyiodo)benzene and fullerene \( C_{60} \) in toluene at room temperature to afford chlorin-fullerenes 1-3 in 52-80 yields.

The effective electron transfer from chlorin to fullerene with a quantum yield of 78\% (for 3), 85\% (for 2), and 90\% (for 1) is realized. The photophysical parameters of electron transfer were defined using spectral and kinetic data. Preliminary data on the generation of active oxygen species were obtained using the synthesized chlorin-fullerenes 1-3.

Acknowledgements
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DEVELOPMENT OF NEW LIPOSOMAL DRUGS

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The intensive development of drug delivery systems based on micro- and nanotechnology is currently leading to the creation of new formulations. Examples of such dosage forms are liposomes which are microscopic, spherical particles filled with the liquid, the membrane of which consists of molecules of the same natural phospholipids as cell membranes. The inclusion of the drug in the composition of the liposomes contributes to the increased tolerance of the encapsulated drug by the patient, but also allows to increase the ratio of therapeutic effect and toxicity of the drug. Liposomes are increasingly being recognized as promising carriers of drugs, because according to the results of numerous clinical trials, the drug in the composition of the liposomes are more effective and less toxic than those used in the free form.

As the drug for inclusion in the liposomes was selected eprinomectin. It is a semisynthetic avermectin derivative, which is a natural compound of macrocyclic lactones family that are used as potent drugs for controlling the internal and external parasites in livestock, pets and humans.

There are a variety methods for the preparation of the liposomes. Thus, unilamellar liposomes containing eprinomectin were prepared from multilamellar vesicles containing various naturally occurring lipids, by ultrasonic treatment. Multilamellar vesicles were prepared using the thin-film method. Then the appropriate lipid mixture and eprinomectin (molar ratio lipid/drug 4:1) was dissolved in chloroform and evaporated to dryness by rotation under reduced pressure at 40°C. The resulting film was hydrated with a buffer solution (pH = 7.4). The suspension containing multilamellar vesicles, was subjected to ultrasonication (power 350 W). As a result of the work done were obtained liposomes containing the encapsulated eprinomectin, having an average diameter of $214.1 \pm 11.7$ nm (Fig. 1) and the degree of the inclusion of 62%.

![Fig. 1. The particle size distribution.](image-url)
Polymeric microparticles are currently widely applied as drug delivery systems. There are several methods used to prepare polymeric micro- and nanoparticles, which can be categorized as chemical and physicochemical methods. In our work, we used the flow ultrasonic disperser.

Objective: to get polymeric micro- and nanoparticles in the flow ultrasonic disperser and to study the impact of process conditions changes on the properties of the particles.

Materials and methods: a copolymer of lactic and glycolic acid (PLGA, 75:25) (the company Evonik Industries, Germany), polyvinyl alcohol (PVA, M 40 000 Da) (the company Chang Chun Petrochemical co. LTD, Taiwan), solvent - methylene chloride. Polymeric microparticles were prepared by one-step emulsification in the flow ultrasonic disperser, followed by extraction/evaporation of the organic solvent. By dint of peristaltic pumps 1% PVA aqueous solution and the PLGA solution in methylene chloride were fed into the channel in which the ultrasonic disperser was installed. The solutions were mixed in the channel and exposed to ultrasonic of the power 600 w. The resulting emulsion is collected in a container mounted on a magnetic stirrer. Stirring was continued for up to 16 hours to allow the evaporation of methylene chloride and the formation of solid microspheres.

Particle size was determined by laser diffraction using a particle size analyzer LS 13 320 Production Beckman Coulter (USA).

Results of the research: The effect of changing the polymer concentration in the organic phase and the changing phase feed rates on the size of the formed particles were studied. Data are presented in Table. Figure 1 shows the particle size distribution.

Dependence of the particle size of the changes of the process parameters

<table>
<thead>
<tr>
<th>PLGA concentration in the organic phase, mg/ml</th>
<th>25,0</th>
<th>10,0</th>
<th>1,0</th>
</tr>
</thead>
<tbody>
<tr>
<td>The feed rate of the organic phase, ml/min</td>
<td>4,0</td>
<td>6,0</td>
<td>8,0</td>
</tr>
<tr>
<td>The feed rate of the aqueous phase, ml/min</td>
<td>106,0</td>
<td>106,0</td>
<td>106,0</td>
</tr>
<tr>
<td>Particle size distribution, nm</td>
<td>$d_1=546,9$</td>
<td>$d_1=390,0$</td>
<td>$d_1=633,0$</td>
</tr>
</tbody>
</table>

![Intensity Distribution](image.png)

Fig.1. Particle size distribution: a - 25 mg / ml; b - 10 mg / ml; c - 1 mg / ml.

The obtained data show that with decreasing polymer concentration in the organic phase particle size decreases. The particle size distribution becomes unimodal. Similar results were observed when increasing the feed rate of the organic phase.
Animal parasitic diseases represent a major scientific and economic problem, which is caused by the prevalence of parasitic diseases that cause great economic losses and damage to health. Farm animals in some regions up to 70-80% are infected with parasites that cause significant reduction in productivity and often death of the animals. To solve this problem requires the development of anthelmintic drugs with high efficacy and safety for the organism. Treatment of parasitic diseases is carried out mainly by foreign drugs or drugs produced in Russia on the basis of imported substances. Therefore, studies are highly relevant for the development of innovative domestic anthelmintic drugs.

We have developed technology of mechano-chemical modification of a number of substances known anthelmintics with hydrophilic polymers, which act as delivery systems for drug molecules (DrugDeliverySystems / DDS /). This solves an important task - to increase the solubility of these substances, which by their nature are classified as bad-and water-insoluble organic molecules. As a result of our technology has improved solubility, permeability, bioavailability and efficacy of these substances led to decrease in the effective dose 5-10 times. In addition, the observed expansion of the range of action of drugs and reducing consumption rates previously used imported substances.

High anthelmintic effect developed systems was achieved by increasing membrane permeability and improved drug delivery of molecules to the active sites of the body corresponding receptors using innovative approaches DDS. The properties of these delivery systems depend on many factors, and is mainly determined by a complex composition such as "host-guest", and production technologies. The advantages of the technology is the ability to produce these complexes for systems that do not have a total area of solubility. Thus, failure in the technology of the use of solvents or melts reduces the likelihood of undesirable side reactions. The proposed technology is scalable and allows to achieve high performance (up to 100 kg per hour of dry matter), it is based on a relatively simple equipment, designed and produced in the Russian Federation and non-waste production. These results open up the prospect of accelerated creation of a broad spectrum drugs having increased therapeutic efficacy and safety on the basis of already authorized for use of drugs. Production of such products will allow for significant substitution of the use of imported drugs.
SPECTRAL PROPERTIES OF SUPRAMOLECULAR COMPOUNDS
BASED ON CHLORINE $\varepsilon_6$

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One of the most important tasks of modern types of photodynamic therapy is the research of physico-chemical properties and biological activity of the novel porphyrine containing objects, such as the water-soluble derivative of chlorophyll - chlorine $\varepsilon_6$ (Ce$_6$). Ce$_6$ is absolutely non-toxical photosensitizer and at the same time anticancer immune response modifier which is strongly activating system of cell-mediated immunity and, especially, K cells, distinguishing and destroying tumor cells. It has the following spectral and power characteristics: the maximum of Ce$_6$ absorption is in area of 660±5 nm that corresponds to area of the greatest optical transparency for biological tissue, and a quantum yield of singlet oxygen reaches 0.7 [1, 2]. Hydrophilia properties, effective transport and accumulation in tumor tissue are provided by having of three carboxyl groups. Nowadays a number of photosensitizers of the second generation on basis Ce$_6$ is applied in clinical practice in Russia. However, these preparations have the high degree of phototoxicity connected with the high quantum yield of singlet oxygen formed under the light influence when carrying out the photodynamic therapy. Besides, chlorine $\varepsilon_6$ as substance, has a number of shortcomings which limit his broad consumption, for example, small period of storage, the loss of optical properties, aggregation of molecules in water solutions that leads to considerable decrease in photodynamic activity. Therefore searches of other, more effective medicines and ways of their receiving continue now.

In this work for the purpose of new medicines creation for photodynamic therapy novel supramolecular systems based on chlorine $\varepsilon_6$ were obtained and their optical absorption and fluorescence were investigated. The influence of different supports as polyvinylpyrrolidone (PVP), polyethyleneglycol (PEG), bovine serum albumin (BSA), chitosan, Triton X-100 (TX-100), sodium hexametaphosphate (GMP), polydimethyldiallylammonium chloride (PDDA) on spectral characteristics of these systems was studied. It is found out that spectral-fluorescence characteristics of Ce$_6$-PVP, Ce$_6$-PEG, Ce$_6$-BSA, Ce$_6$-TX-100, Ce$_6$-GMP, Ce$_6$-PDDA confirm disaggregation of molecules of chlorine $\varepsilon_6$, their consecutive interaction with excipients in solutions and formation of molecular associates and molecular complexes. The system Ce$_6$-chitosan is characterized by aggregation of pigments in solution that reduces photochemical activity of a photosensitizer. The obtained results allow to conclude promising method of controlled aggregation of photosensitizers in the composition of supramolecular complexes to create medicines for PDT of predictable photodynamic activity.

References:
ACRIDIN-9-(10H)-ONES IN THE SYNTHESIS OF BIOLOGICALLY ACTIVE COMPOUNDS WITH A FIVE-MEMBERED HETEROCYCLIC FRAGMENT

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²Kursk State Medical University, Kursk, Russia

Acridine-9 (10H) -ones used for the synthesis of new biologically active compounds. By alkylation of monochloroacetic acid butyl ester they were converted to the corresponding butyl esters of 9-oxoacridine 10 (9H) -yl) acetic acid.

The synthesized acids and their butyl ethers have been used for the synthesis of new derivatives containing units of acridone and five-membered heterocycle.

Acr = 9-oxoacridine-10(9H)-yl

Studies in vitro antibacterial activity revealed substances that have antibacterial and antifungal activity comparable or superior to drugs such as ethacridine lactate and metronidazole. The effect of the substituent in the acridone ring on antibacterial activity of the compound revealed.
UDC 615.225.2

DEVELOPMENT OF INNOVATIVE MEDICINE – INHIBITOR PLATELET AGGREGATION AND STUDY OF ITS PROPERTIES

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2National Research Tomsk State University (TSU), Tomsk, Russia

High death rate and disability from cardiovascular diseases is one of the key problems of medicine. Their share in the total mortality in Russia is 57%. One of the main reasons for this phenomenon is atherosclerosis that develops in the presence of a large number of low-density lipoproteins, which are slightly soluble and prone to allocation in a deposit of cholesterol and to formation of atherosclerotic plaques in vessels.

Platelet aggregation inhibitors (antiplatelet agents) with a different mechanism of actions are used for thrombosis prevention. Due to the limitations and side effects of the application of modern widespread antiplatelet agents, such as Aspirin, Clopidogrel, Dipyridamol, there is a necessity in the search for new means of thrombosis prevention. For this reason the development of the innovative medicine (platelet aggregation inhibitor) and study of its properties was the purpose of this work.

We have synthesized a new medicine representing the indolinone derivative, namely 2-[2-[5-(hydroxymethyl)-3-methyl-1,3-oxazolidin-2-ylidene]-2-cyanoethylidene] indoline-3-on (Fig.) and it is shown in the primary screening test, which has a positive result in the "specific activity" on mice and rats.

![The structural formula of the new antithrombotic drug.](image)

Unlike known antiplatelet agents, the new compound possesses vasodilating, hypotensive action which mechanism involves the formation of nitric oxide, the activating soluble guanylate cyclase, that leads to accumulation of cGMP. The latter activates cGMP-dependent protein kinase, as well as calcium-dependent ATPase participating in dephosphorylation of myosin light chain, resulting in the output of calcium ions from the muscle fibers and ultimately lead to vasodilation.

Synthesized pharmaceutical substance (code name - GRS) represents fine-crystalline powder from orange till red-orange color, odorless, sparingly soluble in methanol and dimethylformamide, slightly soluble in chloroform and almost insoluble in water (SPh XII). The structure and molecular weight of the new compounds have been confirmed by the elemental analysis on «Flash EA 1112 Elemental Analyzer» (Thermo Scientific) equipment, a method of $^1$H NMR on the «AC-300» (Bruker) spectrometer and by mass spectrometry on the ZQ-2000 (Waters) device. To determine the authenticity of the substance was used a method of IR and UV spectroscopy. Also, the following indicators have been developed and defined: sulfate ash and heavy metals, pH, loss in weight on drying, melting point, specific absorption rate (all in accordance with the SPh XII) for quality control. Chromatographic technique on Milichrom A-02 (CJSC «EcoNova», Novosibirsk, Russia) has been developed for the quantitative determination of impurities. A method of potentiometric titration was used for quantitative assessment of the content of active substance.

Thus, we have developed the new medicine - a platelet aggregation inhibitor, and, having preceded preclinical researches, studied its main properties.
A new conjugate of dipeptide OrnHis and ivermectin B1 derivative with potential biological activity was prepared for the purpose of creation of the modern anti-parasitic means having more active therapeutic effect in comparison with the available analogs. Its prospects are fight against parasites in smaller concentration that significantly reduce costs of a course of treatment and also expansion of the range of anti-parasitic drugs.

Currently there is a great need in antihelmintics, to which resistance of parasites isn't developed yet.

Avermectins are effective means against endo- and ectoparasites of plants, animals and humans, however, because of development of resistance parasites, have to find new ways to solve this problem. The modified avermectins have high activity against nematodes, are less toxic and are easier transferred by animals. Thus, the ivermectin (the semi-synthetic substance of avermectins) has a broader spectrum of action, higher efficiency at lower concentration than avermectin.

In this regard, the aim of this work is the synthesis of new potential antiparasitic agents, which conjugate ivermectin B1 derivative and dipeptide (OrnHis) derivative with a terminal triple bond. The synthesis was carried out using the reaction of 1,3-dipolar cycloaddition, which is one of the methods of "click-chemistry", proceeds with high speed, regiospecifically; it is characterized by high yields and mild conditions.

It is supposed that this substance will be more active and can be used in fight against parasites compared with the known means that will allow to reduce significantly preparation cost, and also to expand the range of anti-parasitic means.
CREATION OF NONWOVEN ANTIBACTERIAL COMPOSITIONS ON THE BASIS OF METRONIDAZOLE DERIVATIVES

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Cellulosic viscose textile materials are the most commonly encountered medical dressings in purulent surgery. The immobilization of antimicrobial agent on such a base makes it possible to create new dressing materials having prolonged combined biological effect. In some instances the immobilization of biologically active compounds is conducted by means of d-metal cations complexing on the matrix interface. Heterocyclic organic compounds, the group of imidazoles in particular, are often the active materials. One of the representatives of this group is metronidazole – highly active preparation having wide spectrum of effect in respect of protozoa and obligate anaerobic bacteria.

(2-(5-Nitro-1H-imidazole-1-yl) ethyl 2-(9-tioksoakridin-10 (9H)-yl) acetate (L1), 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 (L2), 2-(2-methyl-5-nitro-1H-imidazole-1-yl) ethyl 2-((4-((2-(2-methyl-5-nitro-1H-imidazole-1-yl) ethoxy) carbonyl) phenyl) amine) benzoate (L3), 2-(2- methyl-5-nitro-1H-imidazole-1-yl) ethyl-(9-akridon-10-yl) acetate (L4), 2-(2-methyl-5-nitro-1H-imidazole-1-yl) ethyl-2-(6H-indole[2,3-b]quinoxaline-6-yl) acetate (L5) – metronidazole derivatives having antibacterial properties. These compounds with cations Zn²⁺; Cu²⁺; Ni²⁺ at рН=3,5-7,5 form complex compounds of various composition: L1-L4 - 1:1, in case of the ligand L5 – with ratio 1:2, due to nucleophilic atom of nitrogen of the imidazole ring in position 3, having the highest possible degree of electron pair localization.

The possibility of application of the active materials on the surface of cellulosic viscose material and its release in simulated solution was estimated by the values of the degree of sorption (R, %) and specific desorption (А', mkg/cm²).

The metronidazole derivatives under investigation do not sorb from ethanol 0,001 mol/dm³ solution onto nonwoven cellulosic viscose material (specs 9393-009-56334457-2010) on exposure within 24 hours. Upon sequential processing of the specimens of nonwoven fabric by solutions of equal molarity of cuprous chloride (II) and L1 – L4 (0,001 mol/dm³), L5 (0,00002 mol/dm³) under similar conditions substantial increase of R was observed (Table). The desorption of active agents from nonwoven matrix into simulated medium with different рН was conducted at a temperature of 37°C within 12 hours. The target values of acidity of the medium were created by adding corresponding aceto-ammonium buffer solutions. As test parameters there were taken А’ values after 12 hours of exposure (Table).

<table>
<thead>
<tr>
<th>L</th>
<th>R_{Cu,Lx} %</th>
<th>A', mkg/cm² at рН</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>88,85±0,40</td>
<td>14,68±0,16 9,17±0,71 18,17±0,16</td>
</tr>
<tr>
<td>2</td>
<td>19,50±0,30</td>
<td>0,41±0,03 0,37±0,05 0,37±0,06</td>
</tr>
<tr>
<td>3</td>
<td>14,80±0,30</td>
<td>0,98±0,02 1,13±0,09 1,10±0,07</td>
</tr>
<tr>
<td>4</td>
<td>95,36±2,51</td>
<td>18,42±0,17 9,13±0,83 17,31±0,15</td>
</tr>
<tr>
<td>5</td>
<td>13,70±1,58</td>
<td>5,30±0,07 7,04±0,04 5,98±0,10</td>
</tr>
</tbody>
</table>

L2 has greater mobility in alkaline medium (А’=26,14 mkg/cm²), for L3 desorption is maximal at pH close to 7 (А’=7,04 mkg/cm²). L1 is better desorbing in subacid (А’= 23,79 mkg/cm²) and in alkalescent media (А’=28,79 mkg/cm²), with this L1 creates the biggest concentration of the active material in consequence of sorption and desorption. Considering the fact that the medium of a suppurative wound is alkaline, the use of the biologically active substance L1 for applications creation offers the greatest promise.
The stress response of the body to exposure to high temperatures fell into the focus of attention of researchers several decades ago and continues to be studied until now. The basis of the thermal shock damaging effect is a disorder of the process of proteins folding. For thermodynamic reasons they increasingly take an abnormal conformation as temperature rises. To compensate for these phenomena a series of chaperone proteins is activated. Their expression increases dramatically during the thermal shock. However, this is not always sufficient. The risk of death of cells and organisms in conditions of hyperthermia is very high. Nevertheless, temperature effects are a promising method of treatment of malignant tumors, which are often less resistant to thermal shock than normal cells. Studies on the thermal stress response, however, have a broader range of applications. Firstly, heat shock proteins function also in normal conditions by controlling the current conformation of proteins. According to some assumptions, disorders related to the functioning of chaperones are among the causes of Alzheimer's and Parkinson's diseases accompanied by abnormal amyloid conformations. Secondly, the heat shock is one of the most severe forms of stress as such. In addition to specific phenomena, such exposure is accompanied by severe oxidative stress damage of biomolecules, including nucleic acids. Obviously, virtually all the other cell-protecting systems are involved in heat shock compensation in addition to chaperones.

The biological activity of 8-oxo-2'-deoxyguanosine was first described in 2006, when a group of Korean researchers showed anti-inflammatory and immunomodulatory effects of this substance. Subsequently, the protective effect of 8-oxo-dG upon irradiation was described. We assumed that it is associated with the ability of this compound to act as a signal for the activation of reparative cells and antioxidant systems. If so, one would expect from 8-oxo-dG activity also in the heat shock model.

The experiment was conducted in Drosophila melanogaster, which is a subject for classic studies of heat shock. For technical reasons the larval stages were selected. Unlike adults they are actively fed and are more sensitive to temperature. Exposure at 37°C for 1 hour on the fifth day of larval development results in a reduction of adults emergence by 60–80% in comparison with the control. Importantly, it is a delayed death associated mainly with lethal disturbances at a later stage, pupa. The larvae of the test groups developed from the very beginning on food containing 1 μM of 8-oxo-dG. According to the results of the experiment, the emergence of adults in this group after exposure to temperature was close to that of intact control. The survival rate of larvae and pupae after heat shock increased approximately by a factor of 5 when 8-oxo-dG was preliminarily added to the food. In this case, the compound is of biogenic origin and, according to our data, does not have toxicity even at high doses. This confirms the potential ability of using 8-oxo-dG as a drug with a wide range of protective activity.
WATER – GLYCERIDE DISPERSE SYSTEMS FOR NEW WATER-SOLUBLE VITAMIN MATERIALS

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Disperse systems composed of biological macromolecules are of great interest for creation of modern technologies for producing colloidal functional materials of new generation. At department of Physics, Chemistry and Technology there is a work on receiving disperse products for the industry and agriculture.

This paper deals with results of work on creation of colloidal forms of water-soluble vitamins for inclusion them on unpolar mediums.

The research is aimed at the development of the principles of creation of nonsaturated fatty acids glyceride colloids from natural vegetable oils with low-speed degradation of water disperse phase. The authors have developed an ultrasonic technique for obtaining of colloidal structures. At the beginning entered water solution of vitamins into glycerides. Used a pyridoxine (В₆) and folic acid (B₉). The relation of volumes of water phase and the glyceride mediums made 1:200. Created an emulsion of water solution of vitamins and glycerides with application of a rotor magnetic mixer. Then this emulsion was processed ultrasound with the use of IL100-6/1 «Ultrasonic technique – INLAB» (Russia). Frequency of ultrasonic waves made 22 kHz. Power – 700 Watt. Applied acoustic waveguide with coefficient of transmission of energy 1:1. The glyceride colloid with water-soluble vitamins were stored in the dark at a temperature of 20 °C.

Dynamics of the disperse phase of vitamin colloid was investigated with the use of the spectrofotofluorimetr CM2203 «Solar» (Belarus). Used quartz cuvette of optical way 1 cm. The temperature in thermostatically controlled cuvette – 20 °C. The light slit width – 2 nm. The colloid was mixed with the application of a rotor magnetic mixer. Operating mode of the device – «kinetics». Studied scattering of light on disperse structures of glycerides with water-soluble vitamins on the wavelength of 730 nm. It is established that on this wavelength vitamins and glycerides do not light absorption. The optical density $D$ in time $t$ of the colloid shows conditions of the disperse phase.

The kinetics were registered about the glyceride medium. In 60 sec placed to the colloid in cuvette compartment. Dependence $D(t)$ was written in the continuous mode, scanning step 0,5 sec. Then the optical density of the colloid determined across 2 h, 4 h, 6 h, 24 hours. The colloid cuvette between measurements were stored in the dark at a temperature of 20 °C.

It is established that the optical density of the vitamin colloid insignificant decreases eventually. The analysis of dependence of optical density on colloid time made it possible to calculate the rate constant of disperse phase degradation, equal to $10^{-6}$ sec⁻¹.

Aggregate and sedimentation stability of glyceride colloids with composition В₆ and В₉ remains a long time, more than 7 days.

It has been proved, that colloids from glyceride of nonsaturated fatty acids with water-soluble molecules (pyridoxine and folic acid) does not result in disperse phase degradation which proves the possibility to develop technologies for obtaining disperse forms of vitamins products.
Drug treatment of patients with coronary heart disease and hypertension – one of the most urgent problems of cardiology. Currently, CPB is the major cause of death in industrialized countries.

In the last decade, considerable interest is aroused by a promising group of potassium channel activators - a new class of drugs, accelerating the movement of potassium ions across cell membranes. Under their influence the muscle fibers relax and the arteries dilate, which leads to improved myocardial blood supply. Drugs of this group are effective for the treatment of stenocardia.

A typical representative of potassium channel modulators is Nicorandil, synonyms - Ikorel, Coronel, Kordinik, Perisalol, Sigmart, Siomart. Nicorandil facilitates the adaptation of myocardium to hypoxia under ischemic conditions. The drug is effective for stable exertional angina and vasospastic angina.

Chemical structure of Nicorandil is N-(2-nitroxyethyl)nicotinamide with structural formula:

![Nicorandil Chemical Structure](image)

This substance was first synthesized in Japan in 1979 and since 1984 has been used as a drug in cardiology. Nicorandil is recommended by European society of cardiologists for patients with stable angina. Nicorandil has been successfully used by cardiologists of Japan and Europe for more than three decades.

The synthesis of nicorandil is based on the following chemical reactions:
1. Preparation of N-(2-hydroxyethyl)nicotinamide;
2. Synthesis of nicorandil by nitration reaction of N-(2-hydroxyethyl)nicotinamide with nitrating mixture of HNO₃/ H₂SO₄.

In Russia and the CIS countries the works in the field of production method development and use of the drug are actively conducted. Formulations for parenteral administration of nicorandil in the counties of former Soviet Union are absent.

The aim of the work is development of production method of N-(2-hydroxyethyl)nicotinamide, suitable for the production of the domestic drug for intravenous administration (injection) on the basis of its formulations. This requires the use of substances of high purity.

The use of nitric acid with sulfuric acid for the nitration mixture does not allow to synthesize the target substance without impurities and by-products.

For these purposes, in the process of nitration of N-(2-hydroxyethyl)nicotinamide we used the mixture of acetic anhydride with concentrated nitric acid. The use of this nitrating mixture allowed to increase the yield and purity of the resulting Nicorandil. The obtained product was characterized by elemental analysis, IR and ¹H NMR spectroscopy and HPLC analysis. It is identical to LGC certificate according to the characteristics.
Today, the industry is actively developing the pharmaceutical industry such as system of delivery drugs. Currently, there are nanoparticles that can deliver a drug into the cell. However, they have low stability and are toxic. Therefore, using vesicular drug delivery systems based on silicon lipoamino. The work aims to develop schemes to obtain cerasome-forming lipids and study of their physical and chemical properties. Synthesis components of cerasomes implemented on the basis of 3-aminopropytriethoxysilane diesters and L-aspartic acid. An important and fundamental process in the creation of structures is the polymerization of the siloxane heads in an aqueous media (sol-gel process). Therefore, the study of the conditions for the sol-gel process is given a lot of attention. To increase the speed of the hydrolysis reaction should be carried out in the presence of an acid or base. In this process, the cleavage occurs radical polymerization of the siloxane network, the occurrence of negative charge. We obtained cerasomes having lower toxicity and higher stability than other means of drug delivery. Using electron microscopy, we were able to take photographs of spherical cerasomes with a small particle size of 170–220 nm.

Acknowledgements

This work was supported by Russian Foundation for Basic Research grant RFBR № 16.04-01010.
Palladium-catalyzed Suzuki cross-coupling reaction of aryl halides with arylboronic acids is an important method for the obtaining of carbon-carbon bonds, in particular for the formation of biaryls, due to the wide variety of functional groups and the low toxicity associated with boronic compounds [1]. There are more than three hundred commercial compounds, which can react the Suzuki, with obtaining of semiproduits of different substances having anticancer and antiviral activity, analgetics and nonsteroidal anti-inflammatory drugs, secondary metabolites of many plants having cytotoxic activity, and substances having antileukemic action. Thus the Suzuki reaction gives possibility to produce compounds possessing strong pharmacological activity which are rarely found in nature [2]. Moreover, Suzuki reaction is used in the synthesis of highly substituted derivatives of styrene [3].

Large diversity of homo- and heterogeneous (ligandless) Pd catalysts has been developed for Suzuki reaction. Although homogeneous Pd complexes generally show higher reaction rates and nearly 100% selectivity towards the desired products in comparison with heterogeneous catalysts, the used ligands are often toxic, expensive and difficult to recover and reuse. Besides, many homogeneous catalysts are also sensitive to oxygen and/or moisture. Furthermore, the contamination of the reaction products with trace amounts of metal represents another major issue associated with the use of transition metal catalysts, and this issue can be particularly important while considering the use of expensive and/or toxic heavy metal complexes. To solve the above issue, significant research needs to be conducted towards the development of new ligandless catalytic systems that can be easily separated and recycled without noticeable loss in efficiency [4].

This work is devoted to the synthesis of Pd-containing hypercrosslinked polystyrene (HPS)-based catalysts and study of their catalytic properties in Suzuki cross-coupling reaction of 4-bromoanisole and phenylboronic acid. Proposed approach is based on the use of porous HPS matrix, which has rigid highly porous structure possessing high mechanical, thermal and chemical stability, as a support for synthesis and stabilization of palladium nanoparticles. HPS-based catalysts were synthesized at variation of palladium content, type of HPS (non-functionalized or bearing amino groups) and nature of the precursor (PdCl2, PdCl2(CH3CN)2, PdCl2(C6H5CN)2 and Pd(OAc)2).

Kinetic study was carried out at variation of type and concentration of base, solvent nature and composition, reaction temperature and gas phase composition. It was shown that HPS-supported palladium catalysts were found to be promising (the conversion of 4-bromoanisole was higher than 98% for less than 1 h of reaction time), simple in preparation and stable for at least four consecutive runs for the Suzuki cross-coupling.

References:
EFFECT OF THE POLYMER MATRIX ON THE PROPERTIES OF FUNCTIONAL POLYMER SOLUTION

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Many polymers have specific properties and may be used in many applications, for example porphyrin polymers. It may be synthesized by reaction of copolymerization of vinyl monomers with porphyrine containing vinyl group on periphery of the macromolecule.

Native methylphaeophorbide \( a \) was used in this investigation as a porphyrine monomer. Methylmethacrylate or glycidylmethacrylate was used as second monomer. The copolymerization reaction was carry out in THF in the presence initiator such as dinitrile of azobisisobutyric acid.

The properties of dilute solutions of methylphaeophorbide \( a \) and methylmethacrylate or methylphaeophorbide \( a \) and glycidylmethacrylate was investigated at 25-35°C in DMF. The intrinsic viscosity \([\eta]\), Huggins constant \( (K_H) \) and root mean square distance between bottoms of polymer were calculated. Root mean square distance between bottoms of polymer was calculated by the Flory-Fox equation.

It is shown that the copolymers of methylphaeophorbide \( a \) and methylmethacrylate or methylphaeophorbide \( a \) and glycidylmethacrylate form systems with lower critical solution temperature.

Also compared the specific index \( <h^2>^{1/2}/M \) for copolymers. This rate degrees with increasing temperature for two composition of monomers.

It is shown that methylphaeophorbide \( a \) have not influence on formation of copolymer properties in amount not more 6-7%.

Acknowledgements

This work was supported by the RFBR (N 15-03-07548).
At the nowadays in the pharmaceutical market there are more and more complex drugs. In creating the conditions for competitive production of liquid dosage forms it is essential scientifically sound quality selection for substances such as solubilizers, surfactants, stabilizers, emulsifiers, and others. One of the main characteristics of the drugs used for preparing injectable dosage forms is solubility in water. Taking into account that ~ 40% of drug substances in accordance with European certified pharmacopeial description practically are classified as well as insoluble, whilst in most cases the most effective route of administration is parenteral, studies to increase the relevance of drug solubility in water, becomes apparent.

To solve this problem it is necessary to realize the optimal choice of solubilizer, it can most effectively be done using information technology.

The effectiveness of experimental studies can be increased by the using the experimental information system (IS), which include a database of bibliographic and reference data that allow us to find the optimal formulation for the production of finished dosage forms of liquid based on choosing a solubilizing agent, for which cyclodextrin derivatives can act as one (CD). Recent form complexes with hydrophobic substances highly soluble in water. Also it can help to solve the economic problems related to the pricing of the finished dosage form and its profitability.

At Plot.1 there are a diagram of IS in IDEF0.
UDC 615.014.23

DEVELOPMENT OF FLOW THROUGH MICRO MODULE FOR PREPARATION OF MICROPARTICLES FILLED BY NALTREXONE BASE

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The primary aims for pharmaceutical formulators are development and introduction of the improved drug delivery systems. Polymeric microparticles with encapsulated therapeutic drugs are the most common pharmaceutical formulas. The conventional methods to produce microparticles are based on the principles of so-called “solvent extraction/evaporation”. Described way of preparation include various laboratory high-speed homogenizers, probe ultrasonicators and impeller mixers. There are some disadvantages for represented method: high cost, low efficiency and difficulty in scaling.

To solve this problem our research group (The department of biotechnology and industrial pharmacy (Moscow Technological University (MITHT)) in conjunction with ZAO «Institute Of Pharmaceutical Technologies») with support from «Foundation for Assistance to Small Innovative Enterprises in Science and Technology (FASIE)» developed flow through micro module for preparation of microparticles by solvent extraction/evaporation method in continuous fashion. The system includes processing chamber, two inlet fittings for feeding of aqueous and organic phases, circulation system and outlet fitting for export of final emulsion. Discharges of organic and water phases are controlled by peristaltic pump. The advantages of the development: low cost and compatibility with general laboratory equipment.

The main components used for preparation of microparticles with encapsulated therapeutic drug in this investigation: model compound – naltrexone base, polymeric matrix – poly (lactic – co-glycolic acid), solvent – dichloromethane (DCM). Aqueous phase included 2% polyvinyl alcohol. According to the experimental studies, we chose feeding speed ratio of aqueous and organic phases 30/ 4 mL per minute respectively. Impeller mixer was used for emulsification and the speed of stirring was 935 rotation per minute. For achievement of lower concentration of DCM and higher encapsulation efficiency, the emulsion was added into 2720 mL water. Final volume of the water was found by series of the experiments. Microparticles mean diameter was characterized via light scattering method, it was 47, 3 ± 3 µm (Fig. 1 b). The encapsulation efficiency was determined by HPLC, it was 74%. Results of scanning electron microscopy have showed the absence of non-encapsulated crystals of naltrexone (Fig. 1 a).

Fig. 1. Resulting particles: (a) Scanning electron microscopy;
(b) Size distribution of polymeric particles.
ANTIBIOTICS PHENAZINE SERIES PRODUCTION AT CULTIVATION BACTERIA
PSEUDOMONAS AERUGINOSA

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At present, one of the actual tasks of biotechnology is to build effective and safe biological crop protection from disease caused by different phytopathogenic microorganisms. The biopesticidal preparations based on natural cultures of microorganisms capable of synthesizing various antimicrobial compounds are considered to be the most effective.

The perspective basis for creating biopesticidal preparations is bacteria Pseudomonas aeruginosa. The different types of compounds synthesized by P. aeruginosa include phenazine compounds and pyridine series. P. aeruginosa can simultaneously form a complex of compounds phenazine series, qualitative and quantitative composition of which depends on the medium components, the cultivation conditions, emission sources and the individual characteristics of the bacterial strains. Phenazines are characterized by a unique mechanism of action and a high antimicrobial activity and the ability to improve penetration of mineral salts in the plant as well [1].

The aim of this work is to identify phenazine series antibiotics and to optimize the cultivation conditions for bacteria P. aeruginosa to increase the yield them.

To obtain phenazine pigments we used periodically cultivating a strain P. aeruginosa on the four media of different compositions medium for cultivation heterotrophic microorganisms PCA (Plate Sount Agar), synthetic minimal medium M-9 (Maniatis et al.), medium King B, used for cultivation of bacteria of Pseudomonas genus and nutrient broth. The bacteria were grown with aeration in Erlenmeyer flasks at 37°C.

Phenazines extraction was performed on the third, fifth and seventh days of cultivation according to the methods proposed by M.E.Levitch and E.R.Stadtman. Cell biomass was separated by centrifugation (5000 rpm) for 15 minutes, the supernatant was acidified (pH 2) using concentrated HCl. Then an equal volume of chloroform was added. The samples were mixed for 30 minutes and centrifuged at 5000 rpm for 10 minutes. The chloroform layer was decanted and then an equal volume of 0.1 N NaOH was added. The samples were mixed for 10 minutes and the chloroform layer was decanted.

The separation of chloroform extracts phenazine compounds was carried out by thin layer and column chromatography. The obtained eluates were studied for the presence of phenazine derivatives by thin layer chromatography with hexane - ethyl acetate (3:2 v/v).

The results indicate that the optimal time of cultivation is five days. In the cultivation liquid is three substances. The separation of phenazine was done by TLC with the solvent system hexane - ethyl acetate (3:2 v/v). TLC analysis showed the presence of three compounds which were separated by column chromatography. Two of the obtained compounds were identified as phenazine-1-carboxylic acid (PCA) and 2-hydroxyphenazine (2-OH P) when spectra were compared with the standard ones. The structure of the third compound has not been established yet.

On the basis of spectral analysis of the resulting phenazines solutions were selected Two mediums in which P. aeruginosa releases the largest number of phenazines. These mediums such as PCA and King B will be modified to provide greater yield phenazine antibiotics. For example, it is known that the use of simple sugars as carbon and energy source, introducing in a medium for microelements cultivation promotes an increased yield of phenazine antibiotics.

Reference:
NOVEL POLYCATIONIC ETHER GLYCEROLIPIDS WITH ANTITUMOR ACTIVITY

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The non-phosphorous cationic ether glycerolipids (CELs) have gained momentum as promising antitumor drug candidates. These compounds are structurally close to the phosphate-containing ether glycerolipid, edelfosine [1]. Importantly, CELs can induce apoptosis of tumor cells without exhibiting a hemolytic effect. The cytotoxicity of CELs is known to depend on lipid structure. In particular, the type of cationic polar head as well as the short and long alkyl chains in the glycerine backbone affect biological activity. Previously, we have synthesized cationic lipids with a high potency to tumor cell lines [2]. In this study, to get insight into the structure-activity relationship in a series of CELs we expanded the library of compounds by varying different structural domains. The charge of polar head was increased by introducing the polycationic groups, that is, natural (spermine) and synthetic (triethylenetetramine) polyamines.

First, we obtained the lipid and the polyamine domains. The lipid derivatives were synthesized by an improved method from rac-glycidol in five stages [3]. The selective protection of polyamine derivatives was performed using different orthogonal protecting groups with subsequent sulfonamide formation. Alkylation of sulfonamide by diglyceride bromides was carried out under the condition of Fukuyama reaction [4]. Finally, removal of protecting groups produced polycationic ether glycerolipids.

The newly synthesized compounds were tested against K562 human chronic myelogenous leukemia and HCT116 colon cancer cell lines. The cytotoxicity depended on the structure of lipid. CELs with ethyl substituted amino group were the most effective against both cell lines. The spermine-based compounds demonstrated a high activity against K562 cells, whereas glycerolipids with triethylenetetramine polar head were preferentially potent against HCT116 cells. The cytotoxic concentrations were within a low micromolar range. These data allowed to identify the lead compounds for an in-depth mechanistic investigation.

Acknowledgements

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References:
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 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 quasiequilibrium 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 technological 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.

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Thiols ability to reversible oxidize and reduction under effect of intracellular glutathione (GSH) underlie the action of variety sulfur-containing drugs. Because photodynamic effect concerned with oxidation of vital organelles of cancer cells by action of reactive oxygen species (ROS), including singlet oxygen, reversing redox-status of intracellular environment on account attrition of glutathione stock under action of photosensitiser (PS) involved disulfide groups, which promote cells sensibilities to oxidative stress and improve effectiveness of photodynamic therapy (PDT).

Based on bacteriochlorophyll a derivative – O-propyloxym-N-propoxybacteriopurpurinimide (dipropoxy-BPI) 1, conjugate with cysteine 2 was synthesized. It which was oxidase on air, give product dimer molecule, containing disulfide bridge (compound 3). Last compound was obtained by counter synthesis interacting dipropoxy-BPI with cystine. Spectral properties and stability in physiological conditions was investigated. Was shown, that disulfide bridge in dimer molecule was reduction by affect of glutathione (GSH), so we can offer the mechanism of the cytotoxic effect of sulfur-containing drug by concentration reduction of reduced form of GSH within tumor cells and reduce their resistance to oxidative stress. High levels of intracellular accumulation of PS and high yields of singlet oxygen in preliminary biological experiments in vitro provide photodynamic efficiency of the compound 3 with nanomolar concentrations of drug.
The synthesis of nanostuctured photosensitizers based on gold and ferromagnetic nanoparticles

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Photodynamic therapy (PDT) combined with drug-delivery agents is a useful technique for cancer treatment. Drug uptake takes place via enhanced permeability and retention effect (passive targeting), as well as receptor-mediated targeting (active targeting). In our study we tried to make nanoconjugates based on golden (Au) and ferromagnetic (Fe3O4) nanoparticles, which posses unique physicochemical properties, such as biocompatibility, thermodynamic and kinetic stability, small size and ease of surface functionality. These constructs can be used as multifunctional platforms for diagnosis (MRI in case of Fe3O4-nanoparticles) and treatment via PDT. In addition golden nanoparticles are widely utilized as agents for photothermal therapy (PTT).

As the photosensitizer (PS) was selected one of bacteriochlorophyll A derivative - O-propyloxym-N-propoxybacteriopurpurinimide (DPBP), what has near-infrared absorption (λmax=800 nm), demonstrated great results during in vivo study and permits deep-seated malignancy treatment. Nanoconjugates were obtained by “pre-load technique” that involves DPBP adsorption on the nanoparticle surface, which is coated by oleic acid and wrapping with pluronic F127. The resulting particles were characterized by dynamic laser scattering (DLS), transmission electron microscopy (TEM), zeta potential measure and spectrophotometry. The hydrodynamic diameter of Fe3O4 nanoparticles is about 95 nm and in the case of Au nanoparticles it is 115 nm. The size of the Au and Fe3O4 nanoparticles by TEM was 12 and 15 nm, respectively. Also we revealed that PS spared it’s photophysical properties unlike in the free state in aqueous media.

Acknowledgements

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SYNTHESIS, STRUCTURE AND BIOLOGICAL ACTIVITY OF CADMIUM IODIDE COMPLEX WITH 1,10-PHENANTHROLINE

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It is known that planar molecules including 1,10-phenanthroline (Phen) are able to intercalate into DNA and destroy it [1]. On the other hand, cadmium compounds possess the ability to inhibit cancer cell growth. That is why the aim of the present work consists in the synthesis of cadmium iodide complex with 1,10-phenanthroline and to study its properties including promising bioactivity.

The complex was prepared in aqueous solution at ~70-80°C by a reaction of cadmium iodide and 1,10-phenanthroline taken in a molar ratio of CdI₂:Phen = 1:0.9. The proposed method of synthesis is simpler and is characterized by a higher yield (> 90% versus 41%) in comparison with the hydrothermal one described in [2].

The prepared [Cd(phen)I₂]ₙ is a white powder, poor soluble in water (its solubility is lower than that of Phen), ethanol, and acetonitrile, and very soluble in DMSO at 25°C. The compound was identified and studied by chemical analysis, powder XRD data, IR-spectroscopy and thermal analysis.

It was found a good compatibility between powder XRD and theoretical XRD data [2] which confirms that the bulk compound and the single crystal have the same structure which consists of one-dimensional chains extending along the c axis. The Cd²⁺ ion is coordinated by two N atoms from one chelating Phen ligand and four I atoms, to furnish a distorted octahedral coordination. Adjacent Cd coordination octahedra share I—I edges, thus forming a one-dimensional chain along the c axis. All Phen ligands are coordinated in a chelating mode and they lie on alternate sides of the chain. The Cd – Cd distance between neighboring Cd²⁺ ions in the chain is 4.2408 Å. The closest distance between the pyridyl and benzene rings of two Phen ligands in neighboring chains is 3.835 Å indicating the presence of weak π–π interactions between adjacent chains. The prepared complex represents the coordination polymer and its polymeric character is confirmed by its low solubility in common solvents and by the absence of melting up to 400°C.

Cytotoxicity of the complex was determined by the MTT-test using the human embryonic fibroblasts HF cells. It has been found that the survivability of cells is about 30-35% at \( c = 1 \times 10^{-4} \) mol/L and it grows up to 90-95% at lower concentration. The lower cytotoxicity of the complex at \( c = 1 \times 10^{-4} \) mol/L in comparison with other cadmium-containing compounds (CdI₂, cadmium iodide complexes with antipyrine and caffeine) is possibly related with lower penetration ability of large species via the cell membrane.

References:
SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITY OF ZINC AND CADMIUM IODIDE COMPLEXES WITH CAFFEINE

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Anticancer activity of zinc(II) and cadmium(II) complexes with a number of ligands has been much investigated [1]. However, to the best of our knowledge, the structural and cytotoxic properties of zinc(II) and cadmium(II) iodide complexes with caffeine remain unknown. That is why the goal of the present work consists in synthesis, identification and cytotoxicity studies of the mentioned compounds.

The complexes were prepared in aqueous solutions by a reaction of cadmium iodide or zinc iodide polyhydrate preliminary obtained from zinc oxide or carbonate and hydroiodic acid. According to [2], the M(I2:Caf (M = Zn, Cd, caf = caffeine) molar ratio was equal to 3:1. The complexes obtained: [Zn(H2O)(caf)I2] (1) and [{Cd(H2O)2(μ-I)2}(caf)-2H2O]n (2) – were identified and studied by a number of methods: chemical analysis, powder and single crystal X-ray diffraction, IR-spectroscopy and thermal analysis.

A good compatibility between powder XRD and theoretical XRD data provide support for the phase purity of the complexes. IR-spectra confirm the coordination of water molecules as well as iodide ions.

Compound (1) is a molecular complex with inner coordination sphere consisting of water molecule, two iodide ions and caffeine molecule coordinated via nitrogen atom. Tetrahedral particles are connected by intermolecular H-bonds involving coordinated water molecules and oxygen atoms of the caffeine molecule from the inner coordination sphere of the neighboring species. It characterized by a non-significant water loss during heating with subsequent caffeine partial decomposition and sublimation.

The cadmium complex [{Cd(H2O)2(μ-I)2}(caf)-2H2O]n (2) is formed by polymeric chains consisting of Cd octahedra with common I-I edges and trans-water molecules. These chains are linked with caffeine and non-coordinated water molecules via intermolecular hydrogen bonds. Upon heating, there are a number of endo-effects due to removal of non-coordinated and coordinated water molecules with subsequent melting and caffeine sublimation.

The results of cytotoxicity studies using the human embryonic fibroblasts HF cells and breast cancer MCF-7 cells demonstrate the dose-dependent effect, the cytotoxicity of cadmium complex (2) being higher with respect to cancer cells in comparison with the normal ones (the minimum survivability being near 40% at the concentration of 1 10^{-6} mol/L).

References:
PHARMACEUTICAL COMPOSITION FOR LUMINESCENT DIAGNOSTICS IN THE INFRARED REGION AND SOME DISEASES TREATMENT MONITORING

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Previously, it was shown that ytterbium complex of 2,4-dimethoxyhematoporphyrin IX (Yb-HP IX) is a perspective fluorescent marker, either as in liposomal forms [1] and water soluble forms [2], for a various tumors diagnostics. The Yb-HP IX has a characteristic for porphyrins tumor tropism and a distinctive intense luminescence signal in the near-infrared (800-1100 nm) spectrum region located in the so-called "tissues transparency window". The Yb-porphyrin complex is highly soluble in water, has a high extinction coefficients values and does not cause adverse reactions in a body due to the lack of photodynamic effect when irradiated with light of wavelength 405 nm.

Continuing studies of this compound in a combination with the portable laser-optic fluorimeter for the infrared region, a pharmaceutical compositions were created for a luminescent diagnostics of pathologically changed skin and mucous membranes, including malignant tumors. The presence of the Yb-porphyrin complex as a part of these compositions allows to effectively monitor carrying out therapy even in absence of visual changes. The pharmaceutical compositions include Yb-HP IX, Tisolum, Cremophor, Kalgel and their mixtures in different proportions, as well as glycerol, N-methylglucosamine additives [3].

It was shown that in the near-infrared region after 40 minutes the pharmaceutical composition accumulation in pathologically changed tissues areas is 3 times higher than in a health areas after the pharmaceutical composition single application on lesions with inflammatory and proliferative processes. During treatment with the inflammation decreasing, the luminescence intensity decreases to values typical for normal tissues.

Thus, the proposed pharmaceutical composition allows to receive information about the accumulation of the Yb-complex and can be used in dermatology, dentistry, gynecology, cosmetology, for ENT-diseases, in veterinary and other medical fields.

Acknowledgements

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THE SYNTHESIS OF NEW PEG-PHOSPHOLIPIDS FOR NANOMATERIALS MODIFICATION

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PEG-phospholipids are applied to modification of various hydrophobic nanomaterials, in particular, of magnetic nanoparticles, the upconversion nanocrystals, gold and silver nanoparticles. Natural derivatives of diacylglycerins, for example, of a phosphatidylethanolamine are most often used. Anionic rest of phosphoric acid in that lipids prevents aggregation of the modified nanoparticles in aqueous solutions.

We have obtained PEG-phospholipid with the polyethyleneglycol-2000 monomethyl ester fragment. To synthesis phosphoric components it was applied H-phosphonate methodology.

This lipid can be applied to formation of a hydrophilic cover on a surface the oleic caped upconversion nanocrystals. More stable alkyl groups will provide the longer time circulation of nanoparticles in blood plasma in comparison with diacyl-PEG-phospholipids.
UDC 577.114.7

TRIVALENT GLYCOLIPID WITH CAPABILITY OF SELF-ORGANIZATION
AND PERSPECTIVE ANTIADHESIVE ACTIVITY

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The adhesion of pathogenic microorganisms, realized by the respective binding of carbohydrates with lectins on the surface of the host cell, is the first step in the colonization and extinction of diseases. Blocking this process will assist to control this interaction that can be applied to prevent infectious diseases. Using the D-mannose derivatives as terminal residues will allow to explore the specific binding with the most widespread of I type pili.

It is known that structure with a hydrophobic component involved ditetradecylloic ester of L-glutamic acids and hydrophilic residues capable of self-organization in the water environment, that create ligands with high density for more effective binding.

The purpose of this work is synthesis of new trivalent glycoconjugate with D-mannose and diester-L-glutamic acid using tris(hydroxymethyl)aminomethan as branching component using effective 1,3-dipolar cycloaddition reaction for further studying of self-organization and anti-adhesion properties.

Acknowledgements

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Ethylene glycol (EG) and propylene glycol (PG) is an important chemical raw materials and widely used in the manufacture of pharmaceuticals, liquid fuel, emulsifiers, surfactants, antifreeze agents, lubricants and solvents, as well as for the synthesis of polyester fibers and resins, such as poly (ethylene terephthalate) and poly (ethylene naphthalate). Propylene glycol is also used for the synthesis of lactic acid, which is widely used, particularly in the production of biodegradable polymers (polylactones) [1]. Since the modern production of glycol based non-renewable petroleum feedstocks and different environmental cleanliness, is urgent to develop new efficient and environmentally friendly ways to produce PG and EG from pulp stocks which are renewable and are large enough to completely cover the chemical industry needs these glycols [2].

In this paper the Ru-containing catalyst on the basis of Fe₃O₄-SiO₂ magnetic nanoparticles (MNPs) was suggested for the process of cellulose hydrogenolysis to EG and PG. MNPs serve as a support for the formation of catalytic complexes or nanoparticles possessing unique catalytic properties due to the large surface area and, consequently, increased number of the active sites.

The experiments were performed in a steel reactor (50 cm³, Parr Instrument, USA). Microcrystalline cellulose, a catalyst and 30 mL of distilled water were loaded into the reactor. Then reactor was flushed three times with hydrogen under 60 bar pressure. The mixture was heated and stirred at 100 rpm. After reaching the operating temperature the stirrer speed was increased up to 600 rpm. This moment was chosen as the reaction starting time. At the end of the experiment the catalyst was separated by neodymium magnet. The non-hydrolyzed cellulose was separated by filtration. Hydrogenolysis process studies were carried out at a temperature varying (205 - 260 °C), hydrogen partial pressure varying (40 – 100 bar), the process time varying (0 - 60 min), and varying the ratio of Ru / cellulose, type of catalyst, the percentage of the ruthenium. The content of the conversion main products was determined by chromatographic methods in liquid phase. For the analysis of a liquid phase highly effective liquid chromatograph UltiMate 3000 (Dionex, USA) was employed.

With the temperature increase the selectivity to PG sharply increases but it decreases smoothly close to 260 °C. The rise of selectivity is not so evident for EG. In all reactions cellulose conversion is 100% and the selectivity to EG and PG are practically the same (≈ 12 and 23%, respectively).

The catalyst is stable under hydrothermal conditions of the process, it is easily separated from the liquid phase with the external magnetic field and can be reused. Therefore, the results of the research prove the advantages of the use of magnetically retrievable catalysts in biomass processing into chemicals and second-generation biofuel.

References:
MODERN TRENDS IN BIO-ORGANOMETALLIC CHEMISTRY

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Modern organometallic chemistry era has begun in 1951, when ferrocene was discovered. R.B. Woodward and A.N. Nesmeyanov, world famous scientists were immediately interested in this unusual iron-containing compound. Intensive research in organometallic chemistry is in highest progress now. Two basic directions are developed: catalytic processes and biochemical and medicinal investigations [1, 2].

Especially ferrocene compounds are at the centre of attention. A large number of ferrocene-modified compounds were investigated as potential antianemic (compnd. 1), antimicrobial, anticancer (2), antimalaria (3), and antituberculosis drug candidates (see Figures). Recently amino acid ferrocene compounds with heterocyclic linker (4) were studied for treatment brain diseases [3].

This is caused by unique properties of ferrocene compounds: stability in biological media, redox activity, lipophilicity favoring easy penetration through cell membranes, low toxicity, diversified modes of their reactions with biological substrates, as well as easiness and variability of chemical modifications and commercial availability. Moreover, modification with ferrocene moiety improves crossing of the blood–brain barrier.

Ferrocene compounds are quite broadly used as amperometric biosensors for proteins, DNA probes, and immunoassay tracers. This became possible due to ideal electrochemical properties of ferrocenes, namely, high rate of electron transfer, low redox-potentials, and chemical stability of reduced (ferrocene) and oxidized (ferricenium) forms. Electrochemical detection is a cheap and high sensitivity method of analysis.

All these ferrocene compounds are technologically available and can be implemented in chemical industry.

Acknowledgements

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References:

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EFFECTIVE AGENTS FOR COMBINATION TUMOR THERAPY BASED ON GOLD(I) THIOLATES

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The combination of the cytotoxic effect of chemotherapy (CT) and angeogennogo effect of photodynamic therapy (PDT) may be a very effective method of preventing tumor formation of different nature. Maximum effectiveness of this combination therapy can be achieved by combining PDT and chemotherapy agents in a single drug.

As the chemotherapy agent was selected triphenylphosphine gold (TPPA) - compound of auranofin group, which mainly accumulates in the cell membranes and is involved in the process of lipid peroxidation. PDT agent was selected diethoxybacteriopurpurin imide (1) is well-established in biological in vitro tests and in vivo. PDT agent was selected dietoksibakteriopurpurin imide (1) is well-established in biological in vitro tests and in vivo. As the sulfur-containing linkers used aminoethanethiol (AET), methyl L-cysteine (CysMe) and L-cysteine (CysMe). Synthesis was carried out in two stages. In the first phase we were synthesized thiolate complexes of cysteine and aminoethanethiol with triphenylphosphine gold (CysMe / Cys-TPPA, AET-TFFA). Thiolate complex AET-TFFA was synthesized for the first time. In the second step, several structural modifications have been synthesized compound (1) with different thiolate complexes (2.3a, 3b, 4). Further biological tests will help to determine the structure-function relationship. The most interest is the thiolate complex 3b, since it has two thiolate complexes, which may significantly increase the cytotoxic effect and block most of the antioxidants in cell, which will increase the overall effectiveness of the drug.
Enzyme activity is largely determined by the reaction conditions, particularly by the pH value. Enzyme demonstrates maximum activity at its corresponding optimal pH. When pH value increases or decreases with respect to the optimum value activity of the enzyme is usually reduced. However, in medicine and in different biotechnological processes there is a need to use enzymes in their suboptimal pH environment. In this regard, the development of new methods for immobilization, which would allow to preserve enzyme activity in suboptimal environments, is one of the biggest challenges of modern biotechnology.

The enzyme kinetics of nanocomposite of proteolytic enzyme chymotrypsin (CT) with selenium (Se) nanoparticles was studied in comparison with the native CT. Se-CT nanocomposite was synthesized in the process of a redox reaction between ascorbic acid and selenious acid in the presence of CT at room temperature and atmospheric pressure. CT concentration (C_{CT}) in the nanocomposite was equal to Se concentration (C_{Se}) and was 2 mg/ml.

To carry out experiments on enzyme kinetics 70 ml of protein substrate solution (sodium caseinate) with a concentration of 10 mg/ml were prepared. pH of the solution was changed by adding different amounts of 1N NaOH and 1N HCl. The solutions were incubated at 37\degree C. From the obtained solution 2 ml were took away as control samples. In the remaining 68 ml of the protein solution 3.4 ml of enzyme solution (nanocomposite) were added. At certain intervals from 2 ml of the reaction mixture were sampled. To interrupt the reaction by denaturing the protein each sample (including the control) was mixed with 3 ml of 0.5N trichloroacetic acid. Then the samples were filtered and the optical density of the supernatant, which characterizes the amount of digested protein, was measured at \lambda=280 \text{ nm}. Results of experiments are presented on the figure.

As can be seen from the figure, the activity of the nanocomposite at pH 6 and 8 is reduced in comparison with the activity of native CT. However, at pH 11 activity of the nanocomposite exceeds activity of CT and differs little from the activity of CT at pH 8. Thus, in case of CT immobilized on Se nanoparticles shift of the pH optimum of the enzyme to alkaline region was observed.

Acknowledgements

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LIPOIC ACID DRUG DELIVERY SYSTEM BASED ON COMPOSITE NANOPARTICLES OF LACTIC ACID COPOLYMERS

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One of the major problems in preparation of topical ocular medicines is a poor water solubility of active compounds. That leads to the reduction of the bioavailability of the drugs. Also, poorly water-soluble drugs are usually rapidly washed out by tear fluid after application and mechanically wiped out by the eyelid. Thus to solve this problem micellar carriers based on biodegradable copolymers are envisioned for use [1], which could facilitate and increase penetration of bioactive poorly water-soluble substances through the cornea making them much more effective.

In this work we take a focus on the mPEG-PLA copolymer. As for mPEG-PLA copolymer, we used mPEG<sub>1000</sub> as a starting material which is manufactured in Russia in large scale and comparatively low price. Also in this work, we present formulation thereof for ophthalmic topical applications with some of the prospective drug candidate lipoic acid [2]).

In this paper, we present a new composite delivery system of lipoic acid based on composite nanoparticles made of copolymer of lactic and glycolic acids Resomer® RG 755S Evonik Industries (Germany) with the addition of the previously synthesized methoxypolyethylene glycol-polylactide (mPEG-PLA) [3] to provide a more stable suspension. For the preparation of nanoparticles with a narrow size distribution we used a specially designed "matrix method", which consists of particles based on PEG-PLA / PLGA containing lipoic acid. Being released from the silicone matrix the particles thus obtained are of the same size, since the matrix has a uniform porosity throughout the entire volume.

On the basis of this composite system we prepared liquid formulation of lipoic acid with an average particle size of ≈ 100 nm and the concentration of active ingredient of 0.8 mg/ml (HPLC). The test samples were put for storage stability studies.

References:
STUDY OF POLYELECTROLYTE COMPLEXES FOR BIOMATERIALS AND MULTILAYER CAPSULES SUITABLE FOR ENCAPSULATION OF ANTICANCER DRUGS

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Anticancer therapy requires new formulations for existing anticancer drugs aiming side effects reduction and dose decrease. Multilayer capsules fabricated via layer-by-layer sequential deposition of polymers onto a sacrificial core template represent a versatile delivery system for a variety of species used in biomedicine [1]. In vivo applications, however, place strict limitations on encapsulating carriers. Among those requirements, biocompatibility, biodegradability, and submicron size that would allow particles to penetrate blood capillaries and somatic cells represent significant technological challenges for the polymer multilayer encapsulation approach. This paper describes our recent developments in fabrication of submicron biocompatible capsules.

The significant obstacle on the way of capsule fabrication is their strong ability to aggregate which is directly related to the capsule’s surface charge and depends on polyelectrolytes used. The next combinations of natural polyelectrolytes have been employed for capsules assembly: bovine serum albumin/tannic acid, polyglutamic acid/poly-L-arginine, dextran sulfate sodium salt/poly-L-arginine, dextran sulfate sodium salt/polylysine, hyaluronic acid/polylysine. The diameter of polymer multilayer capsules is predetermined by the size of sacrificial template used for their formation. Previously we have developed synthesis method of spherical CaCO₃ particles enabling formation of particles in a wide size range from several microns down to 500 nm in diameter [2]. Colloid CaCO₃ particles are widely used templates for capsules assembly [1] and in our experiments we used the smallest 500 nm particles. The best reproducibility and shell stability was obtained for the combination of dextran sulfate sodium salt and poly-L-arginine. These polymer multilayer capsules comprising from 2 to 5 bilayers of this complex maintain their spherical shape, stay unruptured for a long period of time and exhibit low aggregation which is confirmed by a high value of Z-potential of capsules’ surface. Moreover, the technique of temperature induced shrinking of polymer shells (which previously used only for capsules assembled of synthetic polymers [3]) has been optimized. The heat induced shrinking of dextran sulfate sodium salt/poly-L-arginine capsules results in 47±5% decrease of average capsule diameter containing both odd and even number of layers. Designed biocompatible carriers with size less than 300 nm can be potentially used for encapsulation, delivery and release of low molecular weight species including promising photosensitizers and antibiotics with antineoplastic activity.

References:
HYDROXYAPATITE PARTICLES AS CARRIERS FOR $^{223}$Ra

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Alpha-emitters are of the great interest for nuclear medicine due to the high linear energy transfer of α-particles and recoil nuclei. A pathlength of α-particles in biological tissue is much less than that of β-particles and comparable to a cell size (10-100 µm). Being delivered to the tumor cells, α-particles provide its targeted destruction and minimal damage to surrounding organs.

Among various α-emitters, $^{223}$Ra is one of the promising candidates for targeted α-therapy. A radiopharmaceutical Xofigo® on the basis of $^{223}$RaCl₂ is registered and produced by Bayer Company for the therapy of bone metastases. Another approach is a targeted delivery of $^{223}$Ra using various transporters to the cancer cells such as peptides, liposomes or various inorganic carriers. Hydroxyapatite (HAP) particles could be considered as possible carriers of Ra.

Two different approaches to HAP labeling were tested: sorption of Ra on pre-synthesized HAP-particles and insertion of Ra into the structure of HAP during its synthesis. Two textural forms of HAP particles were used – nanoparticles and particles with the diameter of 300±20 µm. Kinetics of sorption of Ra on HAP of different particle size and desorption of Ra in 0.9 % NaCl solution was studied. The influence of solution acidity and solid to liquid phase ratio on sorption of Ra was evaluated and the sorption yield of up to 98% was achieved. It was found that the optimal conditions for the sorption includes synthesis of HAP nanoparticles in the presence of $^{223}$Ra at pH 4-7 and following annealing at 900 °C. In this case subsequent cumulative desorption of Ra is less than 5% of initial activity.

Cross-sectional distribution of Ra inside a HAP particle with diameter 450-550 µm was studied by autoradiography on the plates of polyallulidiglycol carbonate. Kinetics of Ra diffusion into a large HAP particle was estimated.

Using of HAP as carriers is regarded to be prospective for $^{223}$Ra α-therapeutic applications due to the similarity of properties of radium and calcium, as well as bioavailability and biocompatibility of hydroxyapatite.

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Drying kinetics estimation of pharmacopeic Nozepam in pulsed bed

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Pharmacopeic Nozepam is a commonly used anxiolytic agent among benzodiazepines that exhibits pronounced anticonvulsant, sedative-hypnotic and myorelaxing activities. High demand for the drug necessitates its output expansion and further improvement of the production technology including the drying step.

Working out the drying process for the pharmacopeic product in a pulsed-bed pilot setup was reported previously [1]. The effect the operating parameters have on the drying kinetics was determined. A plot for estimating the drying rate during the first period has been derived from the experimental data processing results:

\[ N = 2.78 (w \rho_A)^{0.8} f^{0.4} (H_B / d)^{1.45} (0.026t - 0.36), \]  

(1)

where \( w \rho_A \) is the air mass flow rate (kg/(m²·s)); \( f \) is the pulsation frequency (Hz); \( H_B \) is the product bed height (m); \( d \) is the diameter of the chamber base (m); \( t \) is the temperature of the air and the heating surface (°C). The application of (1) is restricted by the experimental conditions used: \( w \rho_A = 0.88 \text{ kg/(m}^2\cdot\text{s}) \); \( f = 0.5-5.0 \text{ Hz} \); \( H_B / d = 2-4 \); \( t = 50-70 \text{ °C} \). Relative pulse duration \( \psi = 0.5 \).

Figure 1 illustrates a correlation graph of experimental data and calculated data (1) for Nozepam drying rate during the first period.

![Fig. 1. Correlation graph for experiment and calculation via (1) for Nozepam drying rate during the first period.](image)

The relative calculation error does not exceed ±23%. The drying rate during the second period and the total process time were determined pursuant to A.V. Lykov’s procedure, the relative drying coefficient being \( \chi = 0.26 \text{ 1/% as estimated from the kinetic curves.} \)

Reference:
Heparin belongs to the family of glycosaminoglycans (GAGs) endowed with anticoagulant and antithrombotic properties used clinically over the last half-century as an anticoagulant drug [1]. Chemically it consists of repetitive sulfated (–OSO₃⁻,–NHSO₃⁻) and carboxylated (–COO⁻) linear polysaccharide composed of repeating uronic/glucuronic acid and glucosamine residues [2].

Analysis of heparin is challenging due to its heterogeneity, both in its size distribution and charge variance and is of exceptional interest for many researchers [3].

In this paper, the basis for the developing of electrochemical technique for heparin determination by constant-current potential sweep voltammetry was its complexing ability, which is realized by the interaction of the anionic groups of the polysaccharide with cationic groups of other compounds. As the compounds which are capable to form a complex with heparin, the cationic dyes (methylene blue, malachite green, basic fuchsine, toluylene blue) were used. The method of molar ratios was applied to prove the complex formation of heparin with cationic dyes [4].

All electrochemical studies were carried out on the voltammetric analyzer TA-2 ("Tomanalyt", Tomsk) with a three-electrode system. By results of these researches electrochemical techniques of heparin determination in pharmaceuticals have been offered.

Heparin source for the study was a pharmacological solution of high heparin sodium in the form of the tetrasodium salt (Na₄Hep), for internal and subcutaneous administration, production "Moscow Endocrine Plant" - each milliliter of the solution contains 5000 units (1 unit = 0.0077 mg of heparin). During heparin extraction process from mammalian tissue (such as pig intestine), other polyanionic GAGs can co-purify with it since they share heparin-like properties (dermatan sulfate, chondroitin sulfate, oversulfated chondroitin sulfate). For identification of availability of these impurity in the studied drug the capillary electrophoresis method was used [5]. Absence on an elektroforogramme of extraneous peaks testified to purity of the used heparin. Thus one can conclude that on a heparin analytical signal in offered voltammetric techniques nothing affects.

Acknowledgements
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References:
Peptic ulcer is one of the most common diseases. More than 10% of the people over 40 years suffer from this disease. The treatment of this disease is protracted and often requires surgery.

In the opinion of gastroenterologists, De-Nol is one of the most effective anti-ulcer drugs. Pharmacologically active substance of the preparation is bismuth tripotassium dicitrate (colloidal bismuth subcitrate). According to the regulatory documentation for the antiulcer drug De-Nol of the applicant company Astellas Pharma Europe BV (the Netherlands) ND 42-4717-06 (P No.012626/01-131207), the active ingredient of the drug is bismuth tripotassium dicitrate. It is indicated that this is a dried colloidal complex of basic bismuth citrate, potassium and ammonium citrates, with the empirical formula \([\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4]\)\(_n\).

The studies showed that the molar ratio of bismuth ions to citrate ions, potassium and ammonium ions in the substance of De-Nol drug is 1:0.1,4:1:80:1,22, respectively. Hence, the composition of the substance may be represented as \([\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4][\text{K}_3\text{C}_6\text{H}_5\text{O}_7][\text{(NH}_4)_3\text{C}_6\text{H}_5\text{O}_7]\)\(_x\), where \(x=3.2–4.2; y=0.8–1.8\); the percentage of the active component calculated for bismuth oxide is 38.5–42.0%.

It should be stressed that bismuth concentration in the solution obtained by dissolving bismuth citrate \(\text{BiC}_6\text{H}_5\text{O}_7\) in water is only 0.011 g/l, in the case of bismuth tripotassium dicitrate \(\text{BiK}_3(\text{C}_6\text{H}_5\text{O}_7)_2\) this concentration is 1.4 g/l, while in the case of colloidal bismuth subcitrate it is 370 g/l. The resulting solutions were studied by means of small-angle X-ray scattering. The samples were examined by recording transmitted radiation (at the wavelength of 1.516 Å). Processing of the broad peak showed that its position (3.82 deg.) corresponds to the interparticle distance of about 22 Å, and the peak width (3.57 deg.) corresponds to the particle size of ~ 22 Å (~ 2.2 nm).

It is shown that high-purity potassium-bismuth-ammonium citrate can be prepared from metal bismuth which is typically used to synthesize its compounds. The method comprises bismuth purification from accompanying metal impurities through its precipitation in the form of oxohydroxonitrate having the composition \([\text{BiO}_2(\text{OH})_4]\)\(_6\)[\(\text{NO}_3\)]\(_6\)[\(\text{H}_2\text{O}\)], followed by its transfer into citrate having the composition \(\text{BiC}_6\text{H}_5\text{O}_7\) by means of its interaction with the solution of citric acid, dissolution of bismuth citrate in the aqueous solution of potassium hydroxide in the presence of ammonium hydroxide, followed by crystallization during evaporation (65±5 °C) or by spray drying at 230 °C.

Electron microscopic studies of the products obtained by spray drying of the solution and by its crystallization indicate that in the first case the product is composed of the fragments of hollow sphere-like crystals 3 to 100 microns in diameter. In turn, the product obtained as a result of crystallization by evaporation of the solution appears as aggregates 5 to 50 microns in size, composed of elongated prismatic crystals up to 10 microns long and about 2 microns thick, and lamellar crystals 1x1 and 5x5 microns in size, ~ 0,1 microns thick. It should be noted that the product obtained by crystallization of the solution can be well tabletted using water, while the product obtained by spray drying is caramelized and requires the use methanol or dehydrated ethanol at the tabletting stage.

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Kalanchoe is a medical plant, and its extract is often used for treatment of skin wounds, ulcers, burns, and as a biostimulator for skin transplantation. The extract contains valuable organic acids, flavonoids, polysaccharides, tannins, antioxidants, and microelements. The expression of genes of antimicrobial peptides (APs) in these plants enhances their healing and bactericidal properties. At present, APs are considered as effective drugs capable to replace classical antibiotics. APs are the integral part of the innate immune system of all multicellular organisms, demonstrating wide spectrum of bactericidal and fungicidal activity.

At present, genetic engineering methods allow us to synthesize therapeutic proteins in cells of various organisms. Transgenic plants are promising objects for obtaining the recombinant proteins, cheap and safe ones as compared with their traditional producers. The cost of the APs isolated from transgenic plants appears to be 20-30 times lower as compared with other methods of their obtaining. The plants are safer than other producers of pharmacological compounds, because they are free of human and animal pathogenic viruses.

Kalanchoe pinnate (Kalanchoe pinnata L.) plants with synthetic gene of antimicrobial peptide cecropin P1 (cec P1) under the control of promoter 35S RNA of cauliflower mosaic virus (CaMV 35S) were produced. The presence of gene cecP1 in the plant genome was confirmed by PCR. The expression of gene cecP1 in transgenic plants was shown by Northern and Western blot analysis. The produced transgenic plants exhibit enhanced resistance to phytopathogenic bacteria and fungi (Erwinia carotovora, Sclerotinia sclerotiorum and Fusarium oxysporum), while their extracts were characterized by antimicrobial activity against human and animal pathogens (Staphylococcus aureus, Bacillus subtilis and Escherichia coli).

Kalanchoe extract was produced from plant material (leaves) preliminary stored for 7-10 days in a dark at 4°C. After centrifugation at 3000 g for 10 min supernatant was sterilized using the filter 0.22 μm. As a stabilizer 24% ethanol was used. Biological activity of extract and stability of cecropin P1 in it was lasted for 1.5 years. Antibiotic activity of extract retained boiling for 10 minutes. Using model animals, research is running also on application of such extract for treatment of burns and on its hemolytic activity.

Synthesis of antimicrobial peptide cecropin P1 in plants Kalanchoe reinforces the bactericidal properties of this plant and can enhance its value for pharmacology.

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NEW COMPLEXES OF 2-SELANYL-1-PYRIDINE-1-OXIDE WITH METALLS: PRODUCTION AND ANTIMICROBIAL PROPERTIES


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It is well known, that heterocyclic compounds containing chalcogen atoms show extremely varied bioactivity. Nowadays selenium containing heterocyclic compounds are a focus of biological and medical interest because they play a critical role in living organisms’ metabolism. At the same time toxic effects of these selenium compounds especially towards microorganisms haven’t been properly understood yet. Therefore, current research has focused mainly on producing and studying bioactivity of novel selenium containing heterocyclic compounds.

Novel complex compounds were produced through reactions between 2-selanyl-1-pyridine-1-oxide and zinc, copper, cadmium chlorides. Their fungicidal activity was studied. It was established, that bis[1-hydroxypyridine-2(1H)-selonato-Se,O]zinc(II) (1), bis[1-hydroxypyridine-2(1H)-selonato-Se,O]copper(II) (2), bis[1-hydroxypyridine-2(1H)-selonato-Se,O]cadmium(II) (3) were produced in reactions under investigation.

Fungicidal activity of obtained complexes towards fungi which are active decomposers of industrial materials: Alternaria alternata, Penicillium cyclopium, Penicillium chrysogenum, Aspergillus oryzae, Aspergillus terreus, Aspergillus niger was examined. Compound (3) was found to have the maximum fungicidal effect. Our experiments proved that the biocidal activity of the compounds can be regulated. Their toxic effects can be enhanced or reduced by changing the structure of the compounds. To study the mechanism of their toxic activity, ability of given compounds to penetrate and be accumulated in mycelium was determined; in addition their influence on tested fungi exo-oxidoreductase (catalase, peroxidase, phenoloxidase) activity was investigated. It was found visually and by means of scanning electron microscopy that selenium and metals were absorbed on hypha surface and entered fungi cells. Furthermore, it was established that the presence of metals in the molecules of given compounds caused a significant increase in selenium accumulation by fungi cells. Compound (1) was shown to have the strongest inhibitory effect to tested enzymes. These results highlight perceptiveness of further studies of these compounds as fungicides for protection of industrial and structural materials.
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STUDY OF THE STRUCTURE, TOXICITY AND ANTIINFLAMMATORY ACTIVITY OF COMPLEXES OF THE URACIL DERIVATIVES WITH POLYFUNCTIONAL ACIDS

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Pyrimidine bases, in particular, the derivatives of uracil, have been attracting the attention of pharmacologists and chemists for a long time. At present, in medical practice, there used such uracil derivatives as 5-fluorouracil, tegafur, 6-methyluracil, 5-hydroxi-6-methyluracil, methylthiouracilum, propylthiouracil, pentoxy, 3′-deoxi-3′-azidothimidine and others. However, some of the aforementioned drugs, despite of their efficacy, are quite toxic and can cause undesired side effects for the human body. A perspective solution of this problem is the obtaining of complexes of uracil derivatives with higher- and low-molecular polyfunctional acids.

The present work is devoted to obtaining complexes of 6-methyluracil with citrous pectin (I), 6-methyluracil with oxidized fraction of citrous pectin (II) and 5-hydroxi-6-methyluracil with 5-aminosalicylic acid (III) and to studying their structure, toxicity and antiinflammatory activity. The oxidized fraction of citrous pectin (M = 21 kDa) was obtained by ozonization of water solutions of the original polysaccharide (M = 162 kDa) under the following conditions: temperature was 70°C, the feed rate of ozone-oxygen mixture was 6.3 l/h, the oxidation time was 30 min, followed by acetone deposition under the relation of reaction mixture and acetone 1:4.

The formation of complexes I – III was confirmed by the methods of UP, IR and NMR ¹³C spectroscopy. We established that the content of these complexes is equal to 1:1, i.e. for one carboxyl group of polyfunctional acid there is one molecule of uracil derivative. By the method of molar relations we obtained the estimate values of stability constants: K = (2.3 ± 0.2)·10³, (4.2 ± 0.4)·10³ and (12.7 ± 2.2)·10³ l/m for complexes I, II and III, respectively. Values K show quite high strength of the studied complexes. On the base of the obtained results we developed the methods for synthesis of complexes I – III, obtained patterns of these substances and studied their toxicity and antiinflammatory activity.

The study of acute toxicity showed that complexes I – III belong to the fourth class of danger (low-dangerous matters). It is important of mention that complex III is less toxic than one of its components (5-aminosalicylic acid). This example is a good support of the fact that complex creation promote the antiinflammatory activity.

Antiinflammatory activity of complexes I – III was studied by model of acute inflammation caused by introduction of 1% carragenine solution under the aponeurosis of foot. We found that all three complexes have antiinflammatory activity, but the highest activity in comparison with original matters was demonstrated by complexes II and III.

The obtain results demonstrate the perspectivity of the approach based on formation of complexes of uracil derivatives with biologically active polyfunctional acids for creating new medical substances.

Acknowledgements

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DEVELOPMENT OF IMMUNOANALYTICAL SYSTEMS FOR CONTROL OF PHARMACEUTICALS BASED ON FLUORESCENT ORGANIC AND NANOSIZED LABELS

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Active development of pharmaceutical technologies caused extreme widening of the row of substances used in medicine and veterinary. Their uncontrolled use in livestock can lead contamination of food stuffs and risks to human health. In this connection, efficient control of food quality becomes the task of great importance. A species attention should be paid to high-throughput analytical systems for primary screening testing.

Highly sensitive detection of analytes can be achieved through the use of fluorescent labels in combination with immune recognition of target analytes. The given work presents development and validation two kinds of assays for this purpose.

Homogeneous immunoassay for chloramphenicol has been developed using fluorescein as a label. The interaction between specific antibodies and chloramphenicol molecules in the sample is registered basing on the change in degree polarization for the fluorescence caused by the plane-polarized excitation light. The reached limit of chloramphenicol detection was 0.4 ng/mL, detectable concentrations ranged from 6 to 400 ng/mL. Duration of the assay – 10 min. The given fluorescence polarization immunoassay was successfully applied for testing of contaminated dairy products.

The second realized approach was immunochromatographic assay based on the use of quantum dots, semiconductor fluorescent nanostructures. Test-strips for chloramphenicol were manufactured with the use of quantum dots having emission peak at 625 nm. The limit of detection was 0.1 ng/mL, the working range of quantitative assay – 0.2–20 ng/mL. Duration of the assay – 10 min. The possibility to use the developed test strips for control of dairy products has been also demonstrated.

Practical importance of the proposed assays is based on their rapidity and simplicity of implementation. Due to this, wide control of raw materials and finished products may be implemented in food industry, expanding health protection for consumers.

Acknowledgements

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Section 4

Technology of Obtaining Inorganic Materials
For the first time the formation of porous silicon (PS) was described in 1956. The most widespread method of porous silicon layers formation is the anodic etching of a silicon substrate in the solutions contained HF and H2O or C2H5OH.

Nowadays there are a lot of theories to explain the process of PS formation. But they do not suppose any difference between the processes of porous silicon formation on n- and p-types of wafers, while a lot of experimental data show that the mechanisms of the formation of PS on n- and p-patterns are not the same.

A series of experiments have been carried out to investigate the influence of the type of conductivity of silicon substrates on the porous layers obtained under other conditions of experiments being equal. The thickness of porous layers was established to be limited to the value 45-50 \( \mu m \) on p-type wafers and 250-270 \( \mu m \) on n-type wafers as maximum. The layers on p-type of silicon are much more fragile in comparison with ones on n-type.

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 on n-type of silicon wafers, while the pores structured on p-type are of irregular shape.

The sizes of pores depend significantly on the type of conductivity of silicon patterns. They vary from hundreds of \( \mu m \) for n-type PS to tens of nm for p-type PS.

All these facts show that the mechanisms of porous silicon formation on n- and p-silicon wafers possess important distinctions.
Graphite oxide is active material for ammonia gas sensors

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Detection of dangerous and toxic gases is an important field attracting the interests of researchers all over the world. One of these gases is the ammonia, which is classified as dangerous for the environment. Therefore, the development of new gas sensors for its detection is of great importance. Typical ammonia gas sensors are presented by semiconductor gas sensors (based on metal oxides), however, these sensors operate at high temperature (200-350°C) where significant amount of energy is needed for heating. Therefore, the creation of room temperature operated ammonia gas sensors is nowadays problem to be solved.

Carbon nanomaterials such as multi-walled carbon nanotubes, carbon nanofibers used as sensitive material can increase the sensor response significantly [1, 2]. The main disadvantage of theses nanomaterials is the low amount of surface functional groups that makes their treatment unavoidable. The other group of carbon nanomaterials is presented by graphite- and graphenelike materials. One of these materials to be successfully applied for gas sensing is the graphite oxide (GO) [3]. The presence of high content of functional groups on the its surface and within the interlayer space makes the GO sensitive for the polar gases. However, the results of the investigations of GO-based ammonia gas sensors are poorly presented in the papers. Therefore creation of gas sensor based on GO and investigation of their characteristics is of great importance. This work is devoted to investigation of gas sensing properties of GO using as active material.

GO sample was synthesized from pure synthetic graphite (purity 99.9%) using modified Hummers technique [4, 5]. The sample was prepared according to the technique related to sample #3 reported in [5]. The gas sensing properties was measured in ammonia concentration range from 10 to 1000 ppm. The main characteristic that was measured for gas sensors was sensor response (R-R_0)/R_0 (%), where R_0 – sensor resistance in pure air, Ω; R – sensor resistance in ammonia, Ω.

It was obtained that GO based sensor possessed relatively high response to NH_3 (8.0% at 500 ppm) at room temperature. The high value of GO sensor response can be attributed to higher amount of surface functional groups.

References:
SYNTHESIS OF THE EFFECTIVE GTL CATALYST


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GTL (gas to liquid) is the process of obtaining synthetic fuels. This process is beginning to take more and more development in Russia and in particular the search of the effective and stable catalysts in this process. The most perspective are the cobalt-alumina catalyst systems. Recovery to metal of the active component being in the composition of a multicomponent system is an important task since incomplete recovery leads to selectivity decrease to hydrocarbons of the diesel fraction, increase the probability of formation of the inactive cobalt-alumina compounds and the loss of activity due to formation of the condensation products on the catalyst surface.

When the temperature of process increases we have a great risk of formation of the condensation products, but in the same time we have the increasing of selectivity to the formation gasoline and diesel fractions of hydrocarbons. Therefore, there is a strict requirement of selectivity control at elevated temperatures and decreasing the probability of the catalyst activity loss.

The innovative method of synthesis of the effective GTL-catalyst was developed to solve the above problems. The series of cobalt-alumina systems samples was synthesized by the mixing method. Cerium and barium nitrates, γ-aluminium oxide, nitric acid and phosphoric acid were used for the preparation of suspension. The addition of the cerium nitrate have to improve the dispersibility and recoverability of cobalt, and the introduction of barium nitrate is intended to provide the stabilizing effect on transition of γ-aluminium oxide in an inactive form (α-aluminum oxide). Cobalt-containing component was introduced after the homogenization of composition and grinding the resulting mixture. The cured granules were exposed to heat treatment by heating at different end temperatures of 500, 600, 800 °C.

Between cobalt-containing starting components and heat treatment conditions were compared to the final physicochemical and structural and strength properties of the catalyst systems. As the cobalt-containing components Co(NO₃)₂·6H₂O, Co(CO₃)·mCo(OH)₂·nH₂O, and subject to a preliminary thermal activation of Co(CO₃) mCo(OH)₂·nH₂O were used. The preliminary thermal activation of the source component at a temperature above 450 °C for formation of the active fraction nanosized cobalt oxide is required.

As a result of the analysis of the specific surface it was found that using a carbonate leads to the formation of large mesopores. This phenomenon may due to the rapid release of CO₂ as a result of heat treatment and have to provide a high selectivity of the process with respect to the formation of hydrocarbons of the gasoline and diesel fraction.

As it is known, liquid hydrocarbon synthesis process is multidirectional, so in the early stages of research, it was decided to conduct the process of steam reforming of liquid hydrocarbons, eliminates the uncertainty associated with the emergence of new stages of the reactions. By analyzing the results obtained after carrying out the process model, effective degree of surface development samples prepared by cobalt carbonate and thermally activated beforehand embodiment, heat treated at 500 °C was found. These results are consistent with the thermodynamic calculations carried out. After 20 hours of operation under low water vapor content on the catalyst surface a low degree of condensation products formed.
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. 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. To obtain metal complexes we used Ag, Pb, Ca nitrates and REE nitrates hexahydrates.

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.

The syntheses of the complexes were carried out for 24 hours with obtaining of precipitates which were filtrated, washed and dried. First complexes were Ag-lime, Ca-lime, Pb-lime and La-lime. After that we use other bisphosphonates, such as alendronate, pamidronate, neridronate. We obtained La, Ce, Nd, Pr, Sm, Eu, Gd complexes. All complexes were analyzed by the IR, NMR, X-ray and other analyses.

Next step was to 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. We find that the larger carbon chain of the bisphosphonic acid the heavier metal it can precipitate from the solution. By the selectivity data we conclude that bisphosphonates have a promising application in the field of separation of lanthanides. Also they can be used in the field of waste water cleaning from heavy metals, such as Pb, Ca, Zn, Cd.
GENESIS OF COMPOUNDS Cr (III) AND Cr (VI) DURING THE PREPARATION OF CHROMIA/ALUMINA CATALYSTS

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Dehydrogenation of the lower paraffins is one of the most important processes in the chemical industry. With it getting unsaturated monomers it is a valuable raw material for the production of high-octane fuel components (MTBE, alkylate), synthetic rubber, plastics and other products required by modern society. Dehydrogenation catalysts have a different chemical composition and price category, but more than half of the market falls on chromia/alumina catalysts. Numerous studies [1,2] dedicated to this type of catalysts show that chromium on the catalyst surface is in multiple states. Advantageously, this Cr³⁺ (α-Cr₂O₃ and associates Cr³⁺), as well as a certain amount of ions Cr⁶⁺. There is a view that chromia/alumina activity catalysts in a dehydrogenation process are directly related to the amount of hexavalent chromium. Chromia/alumina catalysts is usually prepared by depositing alumina on the carrier CrO₃ and further high temperature heat treatment, during which most of the CrO₃ is converted Cr³⁺. But the mechanism of Cr⁶⁺ occurrence is still not fully understood. Moreover, in the literature state according to the question of the active ingredient of chromium precursor compounds valency in the finished catalyst is poorly represented.

This work has been devoted to the study of the state of the chromium on the surface of the catalyst and the conversion of the original genesis of the precursor compounds. Catalysts were prepared by applying impregnation on microspheroidal [3] and granular alumina carrier Cr(III) and Cr(VI) (CrO₃, Cr(NO₃)₃, Cr(CH₃COO)₃) compounds of their aqueous solutions. After applying the samples were dried in air and then heat treated in an oxidizing atmosphere (air) and an inert gas (helium). Phase changes and the state of chromium in the catalysts by X-ray diffraction, temperature-programmed reduction and differential thermal analysis were examined. The content of hexavalent chromium ions supported in the catalyst by iodometric titration, sulfuric acid and aqueous extracts was determined. Upon dissolution of the catalyst samples were determined in sulfuric acid, the total number of ions, and when dissolved in water - the amount of water-soluble ions weakly bounded Cr⁶⁺. Genesis compounds deposited during the heat treatment compared with the transformation of bulk chromium compounds, heat-treated under the same conditions. The catalytic activity of the samples was studied in the dehydrogenation reaction of isobutane fluidized catalyst bed.

It has been shown that a key factor in the formation of particles Cr⁶⁺ is a heat treatment atmosphere, and that the dependence of their content on the heat treatment temperature applied during the decomposition of the compounds of Cr(III) is extreme. In this specific Cr⁶⁺ content after the final heat treatment temperature for the samples prepared from various chromium compounds differ slightly. Thus, the alumina carrier promotes the oxidation Cr(III) to Cr⁶⁺, which is stable even at high temperatures.

Acknowledgements
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References:
THE PREPARATION OF COMPOUNDS CuAsS$_2$ AND Cu$_3$AsS$_3$ FROM COLLOIDAL SOLUTIONS

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In the system compounds of Cu-As-S are known formulations CuAsS, Cu$_6$As$_4$S$_9$, Cu$_3$AsS$_3$ and Cu$_3$AsS$_4$. These compounds are among the perspective functional materials possessing semiconductor, photoelectric and thermoelectric properties [1–3].

Recently obtaining binary of copper compounds in polar and few polar organic solvents is of considerable practical importance, since the formation of nano- and microparticles occurs very easy. This shows the relevance of fundamental investigation in obtaining compounds CuAsS$_2$ and Cu$_3$AsS$_3$ of ethylene glycol medium.

As initial components for the synthesis of compounds Cu$_3$AsS$_3$ and CuAsS$_2$ were used CuCl and As$_2$S$_3$. CuCl mixed with As$_2$S$_3$ in the ethylene glycol medium in the molar ratios 3:2 (CuAsS$_2$) and 3:1 (Cu$_3$AsS$_3$), respectively and transferred into an autoclave. The synthesis resulted in the temperature interval 353 - 453 K during 48 hours. The resulting precipitate washed several times with 0.1 N nitric acid, ethanol, and distilled water on the order of. Then dried in vacuum oven for 2 hours at 353 K. Conducted microstructure analyzes (HITACHI TM 3000) and determined that nanoparticle is synthesized compounds with high adhesion (Fig. 1).

![Micrograph of nanoparticles compounds CuAsS$_2$ (a) and Cu$_3$AsS$_3$ (b).](image)

The individuality of the synthesized compounds was monitored by DTA (pyrometer STR-70, the device Termoskan-2) and XRD (Bruker D8 ADVANCE, CuK$_α$, $\lambda$=1,5406Å, 0 < 20 < 80°). According to data of XRD and DTA found that at the temperature range 350-400 K is obtained compounds of nanoparticles CuAsS$_2$. These compounds are stable at a temperature below 400 K. It has been established that T>400 K the compound CuAsS$_2$ decomposes. Compounds of Cu$_3$AsS$_3$ melt congruently at 941 K, the polymorphic transformation temperature is 765 K. These data agree well with the literary.

References:
CENTRIFUGAL THERMAL ACTIVATION TECHNOLOGY FOR ACTIVE ALUMINA PREPARATION

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New energy effective technology of preparation of an active alumina via fast thermal treatment of gibbsite in TSEFLARTM reactor of drum type was developed with energy consumption of 1 kWt·h/kg gibbsite, that is twice lower than energy consumption in a similar process of thermal activation in a flue gas flow.

The product of centrifugal thermal activation of gibbsite (CTA GG) Al₂O₃·nH₂O (n=0.20-0.25) is X-ray amorphous and consists of highly dispersed (2-4 nm) aggregated (in pseudo amorphous form) particles. Due to high specific surface area (∼250 m²/g) and defect structure (there is aluminum in fifth coordinated state according NMR ²⁷Al spectroscopy) product possess high chemical activity. So at room temperature it reacts with water solutions forming pseudoboehmite or bayerite depending on electrolyte nature.

A mathematical model that adequately describes particles moving on heated surface of revolving drum, their warm state during heating, reaction and cooling was developed. The model will be useful for reactor scaling up.

Using of CTA GG product instead of flash product (industrial analog) a row of more efficient catalysts (for Clause, dehydration and dehydration process) and desiccants were developed. The possibility of preparation of corundum hollow microspheres based on CTA GG product was revealed.

Acknowledgements
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References:
ELECTROCHEMICAL SYNTHESIS OF ULTRAFINE MATERIALS ON BASIS OF RHENIUM

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In recent years rhenium, its alloys with refractory metals, simple and complex oxides become more and more asked-for in various fields of technology: Re-Mo alloys are used in aircraft and space engineering, bimetallic rhenium-containing catalysts are high-active and selective in motor fuel production processes in which regenerative resources (biomass) are applied. Alkoxotechnology represents promising method for production of rhenium-based materials having required functional properties. The idea of this approach is in hydrolytic or thermal decomposition of mono- and heterometallicalkoxoderivatives of rhenium and d-metals. Electrochemical synthesis of alkoxides is preferable due to its flexibility and technical convenience. It allows to control and fix electrochemical parameters within the wide range and not to introduce impurities into the system. This method corresponds the anodic dissolution of rhenium in the presence of a background electrolyte [1].

Programmed current power supply TDK Lamda GEN 600-1.3 was used in processes of electrochemical dissolution of alloys Electrochemical cell without separation of cathodic and anodic spaces was used.

According to this method the processes of rhenium-nickel alloys anodic dissolution in absolute alcohols ROH (R = Me, Et) with the addition of LiCl were researched and bimetallic rhenium complexes Ni$_x$Re$_y$O$_m$(OEt)$_z$, Ni$_x$Re$_y$O$_m$(OMe)$_z$ etc were obtained for the first time with further investigation of their properties by the methods of IR – spectroscopy and DTA-DTG.

It has been established that the rates of dissolution of the components of alloys Ni-Re (10% mass.) and Ni-Re (20% mass.) in alcohols were essentially different. In first 4 hours (for both alcohols) the dissolution rates of Re and Ni were low and comparable in absolute values. Then the rate of dissolution of nickel was growing exponentially. The speed of dissolution of rhenium was smaller. It is allowed to control the ratio of metals in the crystallization products. It may have a perspective of practical use at obtaining of rhenium alloys and rhenium-nickel alloys with given composition.

Methoxocomplex Ni$_x$Re$_y$O$_m$(OMe)$_z$ [nickel : rhenium = 1:2] was obtained under crystallization of electrolyte dissolution alloy Ni-Re (10% mass.) in methanol at a current density of 0.06 A/cm$^2$. Decreasing of density of a current up to 0.03 A/cm$^2$ leads to crystallization of the product with the ratio of metals 1:2:2. The rate of dissolution of nickel grows when the content of rhenium in alloy Ni-Re (20% mass.) increases twice. The rate of dissolution of rhenium is not changed.

Ethoxocomplex Ni$_x$Re$_y$O$_m$(OEt)$_z$ [nickel : rhenium = 1:4:2] was obtained under crystallization of electrolyte dissolution alloy Ni-Re (10% mass.) in methanol at a current density of 0.06 A/cm$^2$. Decreasing of density of a current up to 0.03 A/cm$^2$ leads to crystallization of the product with the ratio of metals 1:4:1.

The change of electrolyte composition (increasing of the carbon chain in the composition of alcohol) leads to the increasing of the rate of dissolution of nickel and its content in the complexes.

Reference:
Synthesis of the new functional materials – complex chalcogenides, in particular dichalcogenides, opens unexpected new opportunities to study some fundamental problems of condensed matter physics. Dichalcogenides of transition metals, i.e. compounds with the general formula MX2 where M is molybdenum, tungsten or rhenium, etc. and X is a sulfur, selenium or tellurium, are especially interesting.

Majority of chalcogenides are semiconductors and some of them show interesting properties in certain regions of optical spectrum. Such properties allow application of these compounds in optico-electronics, radio-photonics, laser physics etc.

This study contains survey of literature concerning with transition metal chalcogenides in low oxidation states. Analysis of literature data for more than 30 sulfides of transition elements from different groups of the Periodic table shows that the prevalent method of synthesis is annealing of mixtures of corresponding oxides and sulfides or pure elements in vacuum (at temperatures up to 1800°C) or sulfurization in nitrogen atmosphere with carbon disulfide or hydrogen sulfide (at temperatures up to 1300°C).

Known double sulfides of transition elements in low oxidation states crystallize primarily in three structural types – perovskite (BaVS(3-β), BaNbS(3-β)), spinel (BaCu2S2 ) and chalcopyrite (BaCrS2 и etc.). Many sulfides show ferromagnetic properties.

Possibility of existence of perovskites BaMoS3, BaWS3 and BaReS3 is demonstrated and scheme of their synthesis is offered. These compounds are potential ferroelectrics.
PREPARATION OF ZrO₂ AND ZrO₂-TiO₂, ZrO₂-Al₂O₃ OXIDES BY SUPERCRITICAL ANTISOLVENT PRECIPITATION

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Nanoscale materials ZrO₂, ZrO₂-TiO₂, ZrO₂-Al₂O₃ are of interest as catalyst carriers for a wide range of reactions such as oxidation of alcohol, oxidation of cyclohexane, the hydrogenation reaction, the Fischer-Tropsch process. Nano ZrO₂-TiO₂ is used as a photocatalyst of organic matter decomposition; ZrO₂ - as a photocatalyst of water decomposition. The quality depends on the catalyst carrier surface and the porosity of the material. The properties photocatalysts depends on the band gap and the particle size distribution. We used supercritical anti-solvent precipitation (SAS) for producing aforementioned materials. SAS method allows to obtain materials with high surface area and narrow particle size distribution.

We report the synthesis of ZrO₂ nanoparticles and ZrO₂/TiO₂ nanocomposites with different ratio Ti:Zr produced by SAS technique using CO₂ as supercritical fluid. As precursors were used titanium (IV) isopropoxide and zirconium (IV) propoxide. The experimental conditions for the ZrO₂ were varied within the following ranges: pressure between 7,5-25 MPa, temperature between 40-70°C, flow rate CO₂ between 35-50 g/min, flow rate initial solution between 0,25-1,0 ml/min. Composite oxides were prepared by the component ratio 3:1, 3:2, 1:1, 2:3, 1:3. Samples were examined by XRD, DSC and TGA, TEM, Raman spectroscopy. It was investigated influence of synthesis conditions (temperature, pressure, concentration of initial solution, flow rate CO₂ and flow rate solution) on a properties samples such as size, surface area and morphology. Depending on the experimental conditions we got particles in nano-, micro- and shape.

We have suggested options conversion reaction mechanism alkoxide to oxide. Clarification of the mechanism is carried out quantum-chemical calculations of energy barriers, and will be presented in the future.
CHARACTERIZATION OF MICROSTRUCTURE AND CHEMICAL STATE OF ELEMENTS IN Nd\textsuperscript{3+}:Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}/Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} COMBINED TRANSPARENT CERAMICS

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The modern trend in development the diode -pumped solid-state lasers is the use of gain media based on ceramics with the combined architecture, particularly Nd\textsuperscript{3+}:Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} / Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (Nd\textsuperscript{3+}:YAG / YAG) transparent ceramics. This work is aimed to characterization of microstructure and chemical state of elements in Nd\textsuperscript{3+}:YAG / YAG transparent ceramics by scanning electron microscopy, photoelectron and micro-Raman spectroscopy.

4 at.% Nd\textsuperscript{3+}:YAG / YAG combined transparent ceramics (as the model object) were obtained by the reactive sintering method using commercial \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, and Nd\textsubscript{2}O\textsubscript{3} powders as starting materials, and SiO\textsubscript{2}, ZrO\textsubscript{2} as a complex sintering aid [1]. The ceramic samples are characterized by a homogenous microstructure, with no impurity phases revealed at the grain boundaries. According to EDX results of Nd\textsuperscript{3+}-doped layer the composition corresponds to 4 at.% Nd\textsuperscript{3+}:YAG within the method error, indicating effective incorporation of Nd\textsuperscript{3+} ions into YAG host. The diffusion distance of Nd\textsuperscript{3+} ions was nearly 230 µm.

The presence of the following elements in the Nd\textsuperscript{3+}:YAG / YAG structure was defined by XPS analysis of polished surface of the sample: Al, (Y, Nd), O, Zr. The lines position in the Al\textsubscript{2}s (\(E_b=119\) eV), Al\textsubscript{2}p (\(E_b=74.1\) eV), Y\textsubscript{3}p\textsubscript{3/2} (\(E_b=301.3\) eV), Y\textsubscript{3}p\textsubscript{1/2} (\(E_b=312.9\) eV), Y\textsubscript{3}d (\(E_b=158.2\) eV), Y\textsubscript{4}s (\(E_b=45.9\) eV), Y\textsubscript{4}p (\(E_b=26.1\) eV) and O\textsubscript{1}s (\(E_b=530\) eV) spectra of 4 at.% Nd\textsuperscript{3+}:YAG / YAG ceramic surface layers corresponding well with the literature data for \(\text{Cr}^{3+}/\text{Yb}^{3+}:\text{YAG}\) films [2], 2.8 at.% \(\text{V}^{3+}:\text{YAG}\) single crystals and ceramics [3]. The values of XPS binding energies and intensity of the peaks at the study of the polished surface of the sample and of its cleavage are identical. Zr\textsubscript{3}d XPS spectrum shows a sharp doublet according to spin-orbit splitting into Zr\textsubscript{3}d\textsubscript{3/2} and Zr\textsubscript{3}d\textsubscript{5/2} peaks with binding energies of 184 and 182 eV, respectively, which indicates the ZrO\textsubscript{2} bonding [4]. XPS spectra of Nd\textsubscript{3}d\textsubscript{3/2} and Nd\textsubscript{3}d\textsubscript{5/2} peaks, centered at 1005 eV and 982 eV, respectively, confirm that Nd atoms have been effectively incorporated into the Nd\textsuperscript{3+}:YAG garnet matrix and participate in the chemical bonding. The calculated content of neodymium in the sample is equal to 3.9 at.% (the calculation error does not exceed ±10 %). This confirms indirectly the structural and chemical homogeneity of the synthesized 4 at.% Nd\textsuperscript{3+}:YAG / YAG combined transparent ceramics over the whole volume of the sample.

Lattice deformation of 4 at.% Nd\textsuperscript{3+}:YAG ceramic layer with a slight change of crystallites symmetry was revealed (according to the intensity of vibrational motion at 547 cm\textsuperscript{-1} \(\nu_2\) mode of the (AlO\textsubscript{4}) group). Analysis of micro-Raman spectra of 4 at.% Nd\textsuperscript{3+}:YAG / YAG layers showed no significant spectral shifts, indicating their exceptional compositional homogeneity in grains and grain boundaries [6].

References:
Preparation of aluminum oxide nanoparticles often leads to their agglomeration, which adversely affects technical characteristics of materials based on these particles.

Hydrargillite powder was placed into a teflon autoclave inner for the hydrothermal treatment. The treatment was carried out in the acidic medium comprising an aqueous solution of hydrochloric acid at a concentration of 0.08–2.20 wt. % at a temperature of 180–220°C for 4–26 h [1]. The resulted boehmite powder with a particles size of about 50 nm further treated with 10 wt. % solution of ammonium citrate at room temperature on air. Subsequent heating at 800°C for 2–3 hours allow to obtain the γ-Al₂O₃ powder, as well as the heating at 1400°C gives the powder of α-Al₂O₃ with a particles size of about 100 nm. The X-ray pattern proves that the sample contains only hydrargillite phase. Mass spectroscopy shows that the total content of mineral impurities is not more than 0.003 wt. % as the sum of 12 elements.

Not-agglomerated alumina nanopowder may be used as a precursor for the manufacture of catalysts carriers, adsorbents, advanced technical ceramics, etc.

Reference:
At present time the production of sapphire single crystals is carried out by crucible techniques like Chocralsky, Kiropolos, Stepanov methods, etc. In these methods the crystalline alumina is being melted in special crucible before the crystallization. The crucible filling degree has the critical importance for the apparatus productivity.

It was developed the sapphire single crystals precursor preparation method. It includes the following stages. The mixture of hydrargillite and 1 – 15 wt.% of electrically fused corundum must be added to the 0.5 – 2 wt.% hydrochloric acid water solution and stirred until the homogenous distribution of dispersed phase will be achieved. Obtained composition replaced into the autoclave should treated in hydrothermal conditions at 180 – 200°C for 4 – 26 hours. The resulted mixture of formed boehmite and fused corundum must be heated at 1200°C no air in muffle furnace and than fired at 1700 – 1800°C for 1 – 2 hours in vacuum furnace. The product of the method is the ceramic compact with density not less than 3.2 g/cm³ which could be used as the precursor for the sapphire single crystals manufacturing. The developed method allows to produce the precursor with very low level of an impurities, e.g. not more than 10 ppm in total.
THE SYNTHESIS OF SOME HIGH-MELTING CARBIDES

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Industrial usage of carbides of titanium, silicon, chromium and zirconium is based on their refractoriness, high values of hardness, heat conduction, and also stability in corrosive environment. The paper is dedicated to the analysis of the process of synthesis of titanium, silicon, chromium and zirconium carbides by means of carbon nanofibers (CNFs).

The synthesis of carbides of titanium and zirconium was carried out in the resistance furnace with the carbonic heater, and the synthesis of silicon and chrome carbides was carried out in the induction furnace of crucible type in the environment of argon. The level of a completeness of the reactions was defined by comparing of an estimated and an experimental decrease of weight. It has been found that the most appropriate temperature of synthesis of carbides of titanium is 1900-2000 °C, silicon is 1800-1900 °C, chromium is 1300-1400 °C and zirconium is 2000-2100 °C.

The received samples of carbides were researched by X-ray phase and X-ray spectral fluorescent analyses, bottle method, the raster electronic microscopy, the low-temperature adsorption of nitrogen, thermogravimetric and the differential scanning calorimetry. Also determination of the general carbon in the synthesized samples was carried out. Their firmness in solution of sulfuric acid was studied.

According to X-ray phase analysis the products are single-phase and consist of carbides of titanium, silicon, chromium and zirconium. The content of basic elements and carbon is insignificant. The particles have irregular shape and their size is about 3-5 microns. All the particles are partially aggregated. Density of the samples is close to values from reference books. Results of determination of textural characteristics are provided in a Table.

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Temperature of synthesis, °C</th>
<th>Specific surface, m²/g</th>
<th>Specific volume of pores, sm³/g</th>
<th>Mid-diameter of pores, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>1900</td>
<td>2,0</td>
<td>0,009</td>
<td>18,8</td>
</tr>
<tr>
<td>SiC</td>
<td>1800</td>
<td>19,5</td>
<td>0,073</td>
<td>15,0</td>
</tr>
<tr>
<td>Cr₃C₂</td>
<td>1300</td>
<td>1,2</td>
<td>0,003</td>
<td>11,3</td>
</tr>
<tr>
<td>ZrC</td>
<td>2000</td>
<td>2,8</td>
<td>0,009</td>
<td>11,2</td>
</tr>
</tbody>
</table>

High-melting compounds and goods made of them are usually exploited extremal conditions including in the oxidizing environments. Therefore their resistance to an effect of oxygen at the increased temperatures is an important property. Thus at the temperature of 1100 °C silicon carbide doesn’t corrode at all, titanium carbide corrodes partially and the rest of carbides corrode almost completely. All the carbides are resistant to effect of sulfuric acid of concentration 1:4 (the number of insoluble residual is at the level of 99%). So, the received powders of carbides of the micron sizes are comparable in resistance to hostile environment with ocoarse-grained powders of these compounds.

The preliminary technical and economic calculations showed that the price of the received carbides is 2-3 times lower than the prices of foreign suppliers (Goodfellow group of companies) of similar production.
Rapid development of modern organometallic chemistry caused by the ever-growing demand for new materials. Clusters of transition metals are used in many areas. Study and analysis of such systems in recent years the subject of many experimental works. However, the high complexity of the processes of formation of the active sites of these materials prevents getting direct information about their electronic and geometric structure, even in ultra-high vacuum conditions. In this connection, a direct quantum-chemical modeling of the surface of transition metal clusters is designed to provide reliable and fundamentally important structural data, complementing modern experimental research [1].

Previously performed quantum-chemical calculations of the effect of the ligand environment on Re4 cluster, which allowed to understand the nature of the electronic interaction between the ligands and the cluster rhenium. For the quantum-chemical calculation program used Computer Aided Composition of Atomic Orbitals (C.A.C.A.O.) [2].

In this paper, quantum-chemical calculations were carried out under the "Nature", using PBE functional basis and 4 basis, taking into account the relativistic corrections [3,4]. As substitute metal ruthenium was chosen because of the proximity of its properties with rhenium alloy and the potential use of Re-Ni-Ru in the aviation industry. During the calculations it is established that rhenium may be substituted for ruthenium in the complexes where no metal-metal (rhenium metalate complex), and where there is metal-metal bond (rhenium izopropilate complex). The replacements happening in a trance provisions are the most energetically favorable.

References:
The aim of the work is to improve the electrochemical separation method $^{177}$Lu from macroamounts ytterbium. $^{177}$Lu produced by irradiating enriched $^{176}$Yb targets

$^{176}$Yb(n,γ)$^{177}$Yb→$^{177}$Lu. Lutetium-177 is required for biomedical research, as a therapeutic agent for use in radiotherapy.

The separation was carried out by an electrochemical method of contact reduction (cementation) ytterbium sodium amalgam from an aqueous chloride-acetate solutions sequentially in four cells. In the given conditions cannot be restored lutetium. Ytterbium forms an amalgam, passing through the divalent state. Duration cementation process is increased to 30 minutes by adjusting the solution pH in the range pH 4.5-5.5. After four cementation ytterbium concentration decreases in $10^8$ times. Lutetium-177 losses does not exceed 20%. The entire process from cleaning $^{177}$Lu ytterbium and other interfering impurities is not more than four hours. Cleaning method perfected in ytterbium target of several tens of milligrams containing $^{177}$Lu to $10^9$Bk. Lutetium-177 production for advanced cleaning method eliminates the need for the involvement of other separation methods.

Acknowledgements

This work was financially supported by the Ministry of Education and Science of the Russian Federation under in the framework of the Agreement 14.607.21.0041 on "22" July 2014 of the Federal Target Program "Research and development on priority directions of scientific-technological complex of Russia for 2014 - 2020", a unique ID project RFMEFI60714X0041.
Nonmetallic hard-melting materials are widely used in industry because of their high hardness, thermal conductivity, and chemical stability. Silicon carbide is one of the most important materials of this type. He has two crystal modifications: hexagonal (high-temperature modification) and cubic (low-temperature) modification.

Until recently silicon carbide of cubic modification had rather small commercial use. But now the interest has increased because of the use of the silicon carbide as a heterogeneous catalyst. Moreover it can be used as a component of ultra-high-temperature ceramics. Firmness in extreme working conditions makes silicon carbide a very perspective material for such field of technique as aircraft, astronautics and power industry.

Carbon nanofibers (CNFs), which main advantage is high value of surface area (about 200 cm$^2$/g), were used as a carbon material in the reaction of carbothermal reduction. Earlier CNFs were not widely used for the synthesis of hard-melting materials.

The synthesis was carried out in an induction furnace of crucible type in the environment of argon. The duration of the process was about 20 minutes and the temperature was 1800°C. The level of a completeness of the reactions was defined by comparing of an estimated and an experimental decrease of weight. Eventually the experimental decrease of weight was a little more than estimated one. Apparently the reason is the silicon monoxide escape from the reaction zone.

The received samples of carbides were researched by X-ray analysis, the raster electronic microscopy, the low-temperature adsorption of nitrogen, thermogravimetric and the differential scanning calorimetry.

According to X-ray phase analysis the sample is a single-phase material which consists silicon carbide of cubic modification. The content of basic elements and carbon is insignificant. The particles have round shape and their size is about 0.4-0.5 microns. All the particles are partially aggregated.

The sedimentary analysis showed that particles of silicon carbide have a wide range of dispersion that is usual for the materials which are received from chemical reaction. The average size of the particles was 7.97 microns.

The results of the research of textural characteristics of silicon carbide showed that the use of CNFs as a carbon material allows to reach the specific surface size of 19.5 cm$^2$/g. The specific volume of pores was $7.32 \times 10^{-2}$ cm$^3$/g. The mid-diameter of pores was 15 nm.

The preliminary technical and economic calculations showed that the price of the received silicon carbide is 5-7 times lower than the prices of foreign suppliers (Goodfellow group of companies) of similar production.
The ion-exchange capacity of zeolites - one of the main parameters that characterize their sorption and technological properties. The maximum ion exchange capacity corresponds to the complete replacement of the ion in all other positions of the crystal that corresponds to the maximum sorption capacity of the zeolite. The ion-exchange properties of zeolites are determined by the peculiarities of the chemical affinity of the ions with the zeolite crystal structure. In this case, as well as during adsorption of molecules must match the size of the inlet openings in the zeolite skeleton and substituent ions.

By varying the cation composition of zeolites can be a significant impact on their physical and chemical properties. For this reason, the study of ion-exchange properties of zeolites is a hot topic for researchers in many countries. In the literature, information about cation exchange the forms of mordenite it is very limited and mainly concerns their preparation conditions.

The purpose of the work to obtain various cationic forms of zeolite mordenite, these affect the physical and chemical properties of natural mineral, namely, the heat resistance, the temperature of dehydration.

Cation substituted forms of natural zeolite was prepared by ion exchange of a multiple 0,1 N corresponding nitrate solutions at pH ≈ 6, at room temperature and mechanical stirring. The ratio of zeolite: salt solution was 1 : 10. At the end of ion exchange, the zeolites were washed with distilled water until a negative reaction to the salt anion, and dried in air at 373-393 K. The initial weight of the zeolite sample in all experiments was 10 g. zeolitic phase identification was carried out X-ray diffraction (2D PHASER «Bruker» (Cu, Kα, 2θ, 20-80 degrees)), infrared spectroscopy («Nicolete IS-10») and elemental (Oxford scientific) analysis. To reach maximum values of degrees of exchange of the original cations on cations of Mg, Ni, Sr, Zn, Cd sufficiently 50 minutes. A further increase in the duration of treatment has no significant effect on the exchange rate. Values cation exchange degrees K⁺ (αK), contained in the original zeolite cations Mg, Ni, Sr, Zn, Cd is considerably lower than the values of the degree of exchange of the cations Na⁺ (αNa) at the same cations. In this case, the highest value αK achieved in the exchange of cations K⁺ cations Zn²⁺, the lowest - in exchange for cations Mg²⁺. The values of the degree of cation exchange of K⁺ (αK) cations Ni²⁺ and Sr²⁺ are almost identical. The maximum degree of cation exchange K⁺ cations Mg, Ni, Sr, Zn, Cd arranged in the following series: αK→Mg < αK→Ni > αK→Sr < αK→Zn > αK→ Cd. This sequence is also observed for sodium and calcium cations.

From the above it can be concluded that the Zn cation to cation exchange occurs easily and with high speed, and the maximum value of the degree of exchange. The low value of the degree of exchange observed for Mg cations, which due to the high hydration shell magnesium, adversely affect the cation exchange. High values of Na⁺ cation exchange degrees at the first minute of exchange explains low content of sodium cations and their location mostly in available positions for exchange. Less ability to exchange cations K⁺, than the cations Na⁺, contained in the natural zeolite is the result of several factors. As the number of degrees of ionic exchange value exchangeable cations K⁺ vary to a greater degree than the degree of cation exchange Na⁺. Firstly, the content and size of K⁺ cations is greater than the cations Na⁺. Furthermore, part of the cations in the K⁺ is difficult to exchange kankriniovyh cells. These results are explained by the fact that in the experimental conditions indicated cations present in the solution, apparently as aqua-complexes, size and stability of which is mainly determined by the values and degrees of metabolism.
RESEARCH OF PHASE TRANSFORMATION IN THE EMISSION LAYER IN THE MANUFACTURING PROCESS OF THE DISPENSER CATHODE

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Research on the formation process of the emission layer for the dispenser cathodes is of practical and theoretical interest since they are widely used in high-power microwave electric vacuum devices and gas lasers. The increase of dispenser cathode efficiency is possible by formation of the homogeneous oxide formed during the heating of the initial mixture. The aim of this work was to study the phase composition of the initial mixture of BaCO₃, CaCO₃ and Al₂O₃ by heating in a hydrogen atmosphere.

Based on the results of BaO-CaO-Al₂O₃ ternary diagram, it is apparent that a given composition of 2,5BaO·0,4CaO·Al₂O₃ is in the area in which there are Ba₃Al₂O₆ and Ba₃CaAl₂O₇ [1, 2]. X-ray phase analysis has shown that phase and granulometric composition of the initial powder Al₂O₃ has an effect on the fusion process until the temperature reaches 1200 °C, the phase composition of fusion products has little dependence on the phase composition of the starting alumina above the temperature 1450 °C. At the temperature of 1450 °C (Fig. 1) complete decomposition of calcium and barium carbonates occur with the formation of the single phase of Ba₃CaAl₂O₇: 3BaCO₃ + CaCO₃ + Al₂O₃ = Ba₃CaAl₂O₇ + 4CO₂.

References:
Iron carboxylates of unsaturated dicarboxylic acid (UDA) were synthesized: maleic, itaconic, citraconic, acetylenedicarboxylic, glutaconic and cis, cis-muconic ones. The synthesized compounds were characterized by elemental analysis, IR spectroscopy and Mössbauer spectroscopy. As follows from the synthesis a mixture of acidic and medium iron (II, III) carboxylates (AIC and MIC) were obtained. In the case of cis, cis-muconic acid only AIC was formed.

The controlled thermolysis of synthesized AIC and MIC was carried out and obtained nanocomposites were investigated.

Synthesized stabilized magnetoactive metallopolymeric iron nanocomposites, obtained by thermal decomposition under an argon atmosphere, are powders consisting of two structural elements: in organic polymer matrix, in accordance with the data of XRD and Mössbauer spectroscopy, the nanoparticles (NP) of \(\gamma\)-Fe\(_2\)O\(_3\) (cubic symmetry; unit cell parameter: 8.353 ± 0.010 Å, 95% confidence probability) in a polymeric shell of «core-shell» structure are embedded. According to XRD obtained nanocomposites by thermolysis of itaconate, glutaconate and acetylenedicarboxylate of iron (II, III) contain an admixture of \(\alpha\)-Fe (cubic symmetry, unit cell parameter: 2.877 ± 0.026 Å, 95% confidence probability).

The analysis of Mössbauer spectra obtained at 300 K showed that the thermolysis of all iron (II, III) carboxylates leads to the formation of magnetoactive nanocomposites with different phase contribution of ferrimagnetic and superparamagnetic nature. The magnetoactive nanocomposite obtained by thermolysis of iron (II, III) glutaconate is ferromagnetic.

The analysis of Mössbauer spectra obtained at 78 K showed that the iron nanocomposites obtained in the case of thermolysis of iron (II, III) acetylenedicarboxylate in addition to the ferrimagnetic phases of \(\gamma\)-Fe\(_2\)O\(_3\) contain antiferromagnetic phase of \(\alpha\)-Fe\(_2\)O\(_3\). In the case of nanocomposite obtained as a result of thermolysis of iron (II, III) glutaconate a Mössbauer spectrum contains the ferrimagnetic phases \(\gamma\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\).

The enthalpies (\(\Delta H_r^0\)) of formation reaction of acidic and medium iron (II, III) carboxylates were calculated by using the HyperChem 8.0.8 software (Hypercube Inc.) and the PM3 semi-empirical quantum-chemical method.

The size distribution of nanoparticles and their average diameter (\(d_{avg}\)) were determined by using the LabVIEW 8.5.1 software for the automatic processing of electronic micrographs. Obtained \(d_{avg}\) are within of 5-7 nm.

The relationship between the \(d_{avg}\) and \(\Delta H_r^0\) of acidic and medium iron (II, III) carboxylates was established.

The microstructure and magnetic characteristics of the synthesized nanocomposites were determined. The highest coercive force (119 Oe) and highest maximum residual magnetization (5.9 emu/g) is observed for the nanocomposites prepared through the thermolysis of iron itaconate (II, III). The highest maximum magnetization (37.8 emu/g) has been fixed for the nanocomposite prepared through the thermolysis of iron citraconate (II, III).

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NANO-SiC SYNTHESIZED IN A HYPERSONIC PLASMA JET OF A COAXIAL MAGNETOPLASMA ACCELERATOR
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Silicon carbide is one of the most important non-oxide materials and it is a very attractive material for a wide range of industrial applications. Nanomaterials are known to have unique and higher properties than conventional materials. Various silicon carbide nanostructures are widely used as ceramics reinforcement, for creation of nanostructured ceramics, micro- and nanoelectromechanical systems (MEMS and NEMS). Carbothermal reduction, physical vapor transport (PVT), self-propagation high-temperaturesynthesis (SHS), chemical vapour deposition (CVD), sol-gel methods, gas-phase reaction method are the most widely used methods for nano-SiC production.

Nano-SiC synthesis can be realized in the hypersonic plasma of 11-28 kJ. The aim of this work is to implement nano-SiC synthesis in a free expiring hypersonic plasma jet and evaluate the effect of plasma energy on nanosized product characteristics.

The method is based on the use of a coaxial magnetoplasma accelerator of a Z-pinch type as a plasma jet generator. Silicon and graphite micron-sized powders were applied as precursors directly into the plasma jet. The experiments were carried out at different values of supplied energy (capacity 6 mF, charging voltage 2-3.5 kV, process duration was ~300 μs). The synthesized nanopowders were investigated by X-ray diffractometry XRD (Shimadzu XRD 7000 diffractometer, CuKα radiation) and transmission electron microscopy TEM (Philips CM 30 transmission electron microscope) without any preparation.

The XRD and TEM results present primary formation of nano-β-SiC up to 95 wt. % and residual silicon and graphite. According to quantitative analysis the nano-β-SiC fraction weight increases when plasma energy rises. It can be explained by more complete reaction between Si and C due to increasing temperature and pressure in the head part of a plasma jet. Energy change has no influence on SiC particle size, values of coherent scattering regions and particle size distribution. It is associated with the fact that free expiring plasma jet does not create a quasistationary mode within a very short time (~300 μs). Thus, the possibility of long-term particles growth was not implemented as opposed to experiments with expiring plasma jet on a target [1].

The nano-β-SiC was produced by synthesis in the hypersonic plasma jet. Nano-β-SiC content grows and particle sizes remain constant with the increasing of the plasma jet energy.

Reference:
Thermal-barrier coatings (TBCs) are refractory-oxide ceramic coatings applied to the surfaces of metallic parts in the hottest part of gas-turbine engines operating at elevated temperatures [1]. The yttria-stabilized zirconia (7YSZ) is the most commonly used as the thermal barrier coating materials for turbine engines. But currently there is a continuous search for an alternative oxide material to the 7YSZ. The new material should have low thermal conductivity, high temperature stability, and ferroelastic toughening as exhibited by the 7YSZ [2, 3]. The system $\text{ZrO}_2$-$\text{Ta}_2\text{O}_5$-$\text{Y}_2\text{O}_3$ has attracted attention due to the fact that its compositions can be used as components of the TBC coatings.

The powders were synthesized by using of Low hydrated hydroxides (LHHs) of zirconium, tantalum and yttrium as precursors. LHHs were prepared by a heterophase process, by reacting chlorides (oxochloride in the case of zirconium) with 6.0–9.5 M aqueous ammonia. It yields hydroxides with relatively low water content (~ 20-30 %), which can be easily filtrated. These hydroxide phases possess high reactivity and sorption ability. The main advantage of this technique is in obtaining samples with improved technological properties and high metal oxide content (over 67.8 wt.% in the case of zirconium, 87.1 wt.% in the case of tantalum and 62.7 wt.% in the case of yttrium). The chloride ion content in the synthesized LHHs hydroxide was less than 0.05%. The probable sequences of LHHs thermal decomposition stages were proposed on the base of differential thermal and X-ray diffraction analyses results obtained at ambient pressure.

We investigated the compositions along the binary line $\text{ZrO}_2$-$\text{YTaO}_4$ in the system $\text{ZrO}_2$-$\text{Ta}_2\text{O}_5$-$\text{Y}_2\text{O}_3$. For synthesis $\text{Y}_{1-x}\text{Ta}_{1-x}\text{Zr}_{2x}\text{O}_2$ ($x=0.2$ and 0.8) LHHs were mixed in the necessary mole ratio, then distilled water was added to the mixture. The resulting suspension was stirred on a vibrating apparatus and then dried at ~200°C until a dry powder was obtained.

Then, heat treatment was carried out stepwise in the range 200–1000°C in 200 °C steps. The product was a fine-grained powder.

X-ray diffraction analysis was carried out for samples annealed at temperatures 400, 750 and 900°C. In all samples, the formation of two phases – yttrium tantalate and solid solution based on zirconia (cubic modification) – was discovered.

Acknowledgements
This work was supported by the Russian Foundation for Basic Research, project No. 15-03-04436.

References:
LUMINESCENCE AND COATING PROPERTIES OF Gd(III), Eu(III) AND Tb(III) COMPLEXES WITH 4-DODECYLOXYBENZOIC ACID


Complex compounds of lanthanides with aromatic carboxylic acids has an efficient luminescence in the visible spectrum. But most of them are not soluble in organic solvents, which further complicates their application. Introduction of alkyl radical into benzoic ring of ligand should lead to an increase of solubility of complex compounds in nonpolar organic solvents and to formation of amorphous films.

In this regard we synthesized complexes of gadolinium(III), europium(III) and terbium(III) with 4-dodecyloxybenzoic acid. The ligand was obtained in two stages: at the first stage 4-dodecyloxybenzaldehyde was synthesized by reaction between dodecylbromide and 4-hydroxylbenzaldehyde, at the second stage the resulting aldehyde was oxidised by the Jones reagent with the temperature below 50°C. The resulting acid was filtered and dry at 80°C.

Complex compounds were obtained by reaction between resulted acid and lanthanide(III) chloride in a weakly acid medium with a yield about 70 - 80%.

All compounds are white precipitates that are well soluble in chloroform. Composition of complexes was calculated by results of the thermal analysis, overall formula was LnL₃·H₂O (Ln³⁺ = Gd³⁺, Eu³⁺, Tb³⁺; L⁻ = ion of 4-dodecyloxybenzoate). The metals contents was analyzed by complexometric titration. Bidentate coordination was found by IR-spectroscopy.

Triplet state of ligand (20290 cm⁻¹) was found by emission spectra of gadolinium complex. Investigation of photoluminescent properties of terbium(III) and europium(III) compounds showed that integral intensity compared with corresponding benzoates is 1,5 times greater for terbium(III) complex and 4,3 times greater for europium(III) complex.

Coating properties of obtained compounds were studied with terbium(III) complexes. Substance has been dissolved in chloroform and coated to rotating glass sample, that previously was carefully cleaned. To compare the films quality thin films of terbium(III) 2-benzoylbenzoate were similarly obtained. The quality of the resulting films was preliminarily evaluated for their uniformity of luminescence, achieving uniform illumination over the entire area.

The most homogeneous films were studied in more detail by scanning electron microscopy. The film of terbium(III) 2-benzoylbenzoate had a lot of crystalline inclusions, while the film of terbium(III) 4-dodecyloxybenzoate had no defects, that shows better coating properties for the second. Presumably better coating properties of complex with 4-dodecyloxybenzoic acid due to the presence of long alkoxy chain in the structure of ligand.
ON THE POSSIBILITY OF COMPLEX PROCESSING OF RARE-EARTH-RARE-METAL ORES BY COMBINED HYDROMETALLURGICAL AND PYROMETALLURGICAL METHODS

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Complex processing is the most important principle of all mineral commodity department industries, is used to separate minerals into final products by removing all valuable components contained in the feedstock at all stages of processing, but complex processing is also essential value to intensify the industrial production of metals.

The research on complex processing were carry out on the rich niobium-rare-earth ores of one deposits of Siberia. The samples of ore formation of the studied deposits characterize mineral species differing by significant fluctuations of niobium oxide (from 0,18 to 1,73 %), REO (La2O3 from 0,16 to 2,55 %; CeO2 from 0,34 to 3,33 %), manganese oxides (from 2,92 to 27,12 %), iron oxides (31,80 to 68,52 %) and ratios of ore and rock-forming minerals.

The object of the study was initial ore sample of size -0,071 mm composition, %: MnO – 8,80; P2O5 – 4,95; Fe2O3 – 54,24; Nb2O5 – 1,49; ∑REО – 2,09; ThO2 – 0,02; Y2O3 – 0,15.

During the experimental researches it is established that the optimal parameters for processing samples is a two stage autoclave leaching (C HNO3=25%; t1stage=160 °C, t2stage=230 °C; duration - 2 hours; S:L=1:4) with the introduction of the solution for decomposition the hydrogen peroxide. Carrying process in the specified condition provides the extraction in solution of 44,5% ∑ REO (La2O3, CeO2, Nd2O3), manganese – 90%, in the filter cake from the leaching concentrates 70 – 75% Fe2O3 and P2O5, niobium remains completely in the insoluble cake.

To extract Nb2O5 from the cake of acid leaching was used the method of fusing with sodium hydroxide. The fusion with sodium hydroxide was carried out at a weight ratio of niobium-containing keck and alkali 1:3. A mixture of NaOH and a cake was kept at a temperature of 800 °C during 1 hour. After of holding at the maximum temperature the melt was granulated in water, crushed and leaching water at a temperature of 80-90 °C at the ratio S:L=1:3. Strongly alkaline solution containing the bulk of the impurities (phosphorus, silicon, etc.) was separated by decantation, the resulting residue was washed with hot 5% sodium hydroxide solution to prevent the transition of niobiunin a solution. The obtained niobates of sodium decomposed by 18% solution of hydrochloric acid at a ratio of S:L=1:4. The solid residue (hydrated niobium oxide) was repeatedly washed from salts of iron with hot water, acidified with hydrochloric acid. The obtained niobium pentoxide contained 98,5% of Nb2O5.

Thus, the conducted research showed the possibility of combining pyrometallurgical and hydrometallurgical methods with the aim of improving the complexity, completeness of processing rare-earth-rare-metal ores and investment attractiveness of the field.
THE EXPERIMENTAL INVESTIGATION OF THE ETCHING COMPOSITIONS AND ANALYSIS THEIR USE FOR SEMICONDUCTOR COMPOUNDS $\text{A}^\text{II}\text{B}^\text{VI}$

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Currently, most popular photodetectors (FD) and the matrix photodetectors (FDM) large format in infrared (IR) optoelectronics. One of the most widely used materials for FD and FDM-IR spectrum remains CdTe and solid solution Cd$_x$Hg$_{1-x}$Te (MCT), due to the peculiarities of its fundamental properties. Changing the composition of the solid solution Cd$_x$Hg$_{1-x}$Te, you can optimize the sensitivity of FD and FDM on its basis for the basic ranges of the infrared region in the windows transparency of the atmosphere: 1-3, 3-5, 8-14 microns.

Modern FD and FDM on the basis MCT achieve high quantum efficiency (~100%), have a fairly uniform distribution of the composition on the area of epitaxial structures ($\Delta x=\pm 0.002$) and have a large radiation resistance. Today the main problem is to manufacture matrixes larger formats on the basis of the MCT with the uniformity of the sensitivity of its elements in the focal plane and high photovoltaic parameters. The solution to this problem imposes certain requirements on the epitaxial material for heterojunctions and multilayer structures, of which produce the matrix photodetector. The main requirement is the minimum number of growth defects and structural defects in worker epitaxial layers of the MCT.

The results of the study of surface morphology of epitaxial heterostructures on the basis of the MCT, was obtained by the method of optical differentiation-contrast and electron-ion microscopy after selective etching. Heteroepitaxial structures based on MCT grown by means of molecular-beam epitaxy on GaAs substrates with the orientation [310]. Was used etching composition based on chromium oxide (VI), acidified with hydrochloric acid. To improve the quality of selective etching the surface of the heteroepitaxial layers in the etching process was added a various of organic acid to the based solution to obtain more precise figures etching. To obtain the triangular etch pits etching treatment time in the solution was about 30-45 seconds.

Shows the distribution of the dislocation density on the surface of a piece (plot) of the original heteroepitaxial layers on the basis of the MCT. The fragment is divided into squares with an area of 10×10 $\mu$m$^2$. The number of dislocations marked in each square (the color denotes the limit value of the number of dislocations for each square). The density of etching pits on different samples ranges from $3\times10^6$ to $8\times10^6$ cm$^{-2}$. This is valid for heteroepitaxial layers based on MCT grown on substrates of gallium arsenide.

Application polishing solution on the basis of bromatology acid in combination with selective solution made it possible to observe dislocation loops in epitaxial layers MCT. Shows electron microscopic image of the surface of the epitaxial layer MCT after alternate etching processing in selective solution and polishing solution.

For epitaxial layers of MCT is most characteristic of the development of dislocations of mixed type with a predominance of the screw component and the dislocation loops at a typical density of dislocations in MCT layers (on GaAs substrates) the order of $10^5-10^6$ cm$^{-2}$. On dislocation loops growth occurs via a layer-spiral mechanism. Along the dislocation lines is a segregation of impurities in the growing layers. Therefore, screw dislocation, especially dislocation loops, cause three-dimensional growth, which leads to the formation of mounds. The mounds can also cause pinning of precipitates of tellurium and formation of V-defects.
Oxidation reaction of chloride ions by oxygen in molten chloride mixes ZnCl₂ and NaCl:

\[
\text{ZnCl}_2\text{(molten)} + \frac{1}{2} \text{O}_2\text{(gas)} \leftrightarrow \text{ZnO}\text{(solid)} + \text{Cl}_2\text{(gas)}
\]

at various contents of ZnCl₂ in the melt has been investigated. Portions of chlorine and zinc oxide formed were evinced to be dependent on concentration of zinc chloride in the melt.

The rate constants of the zero-order oxidation reaction of chloride ions were calculated with respect to chlorine. In the ZnCl₂-NaCl system, the oxidation rate of chloride ions is below as compared with that in the ZnCl₂. At concentration below than 40 mol.% of ZnCl₂, values of the amount of chlorine produced in the melts of ZnCl₂-NaCl are sharply fallen.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>ZnCl₂, mol.%</th>
<th>ZnCl₂-NaCl melt, ( k_o \cdot 10^8 ), mol/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>2.75 ± 0.41</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>3.58 ± 0.34</td>
</tr>
<tr>
<td>3</td>
<td>67 (eut)</td>
<td>4.81 ± 0.65</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>20.35 ± 0.18</td>
</tr>
</tbody>
</table>

The oxidation process of chloride ions at low concentrations of ZnCl₂ (lesser 40 vol.%) was ascertained to limit the diffusion rate of oxygen at the gas-melt interface.

Particles of the educed ZnO are sized 1-4 μm on average, besides, the specimens contain particles sized lesser 1 μm and over 4 μm.

Acknowledgements

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DILATOMETRIC RESEARCH IN THE "CERAMIC-GLAZE" TO REDUCE THE STRAIN CERAMIC TILES

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The lack of compatibility between the glaze surface and the ceramics substrate is one of the major causes of defects in ceramics processing. When no compatibility in the thermal expansion exists between these two parts of a ceramic tile, defects like chipping, curvature, deformation and cracks can occur.

During firing the glaze selectively reacts with the substrate, forming an interface between both that can considerably affect the stresses acting on them as a whole. The composition glaze changes due to reaction with the substrate in function of the volatilization of certain elements. At the same time, the substrate texture, due to changes in its porosity, and mineralogical composition are modified. All of these influence on the deformation of ceramic glazed tiles.

The aim of this study is to investigate the influence of dilatometric and technological characteristics of ceramics and glazes on the deformation of glazed tiles.

The results of the study indicate that the deformation mechanism of ceramic tiles using glazes is complex. There is a sample tiles bending towards the concavity in the initial stages of sintering at relatively low temperatures. This is probably due to the fact that the expansion of the ceramic mass over the rear side due to shrinkage and temperature differences compared with the surface layer, because the glaze covers the ceramic body, and has a thermal insulating effect. This character is preserved up to temperatures of 600–700 °C and there is a change of character with a concave deformation on the convex. This is probably due to the fact that, in the firing temperatures crock expansion decreases (according dilatometric studies) as well as the icing closes crock, the underglaze layer temperature is lower compared to the rear and, respectively, the surface layer continues to grow.

With the gradual increase in temperature and transition glaze pyroplastic state, the convex deformation decreases and is replaced by concavity. This is due to the beginning of glazes sintering (870–930 °C as determined by heating temperature microscope), occurrence of the first liquid phase droplets, the further reduction of its viscosity and interaction with starting ceramic crock. Under these conditions the reactive liquid phase begins to react with the ceramic crock, gradually penetrates into it and making it more active as compared with the back side. In this period, the shrinkage of the surface layer, coated with glaze, significantly higher than shrinkage of ceramic crock that uncoated of glaze, i.e. the back side. At the maximum firing temperature corresponding active sintering of ceramic mass, the deformation is amplified due to the action of its own weight of the tiles.

The mechanism described above is allowed to assume that the deformation of glazed tiles is primarily determined by the interaction of the processes of the ceramic crock and glaze coatings, which, in turn, is directly dependent on the technical characteristics of the coating applied.

Deformation of samples, coated by opacified glaze, is below in compared with samples decorated using transparent glazes. It’s due to the fact that the transparent glaze has a large amount of glass, while in the opacified glazes crystallization processes actively develop and a lot of amount of crystalline phase is present.

It was found that when decorating ceramic tiles by more refractory and viscous glaze the products less subject to deformation in compared to less viscous glazes. This is probably due to the fact that the last melt at a lower temperature, respectively, they are longer and more responsive interact with ceramic crock, which in turn leads to an increase in facial layer shrinkage and promotes bending of the tiles in the direction of concavity.
THE USE OF ULTRASONIC PROCESSING FOR SYNTHESIS OF GRANULATED BINDER-FREE LTA ZEOLITE FROM METAKAOLIN

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It was studied the influence ultrasonic processing (22 kHz) of an aqueous suspension of metakaolin on the synthesis of the granulated binder-free LTA zeolite. Mixtures with a molar ratio of the solid ingredients of $6\text{Al}_2\text{Si}_2\text{O}_7: 12\text{NaOH}$ (stoichiometric) and $6\text{Al}_2\text{Si}_2\text{O}_7: 12\text{NaOH}: 2\text{Al}_2\text{O}_3$ have been investigated. XRD, SEM, FT-IR and rotational viscosimetry have been used for testing. It was established that in the mixture with an $\text{Al}_2\text{O}_3$ excess after the ultrasonic processing, sodium aluminates of cubic syngony were synthesized. Moulding pastes have been prepared from the sonicated suspensions and pellets of 3 mm diameter have been formed by extrusion.

It is shown that sodium aluminates increased both the strength of coagulation structure of pastes and the mechanical strength of the pellets. It was found that after the thermal treatment of the granules at 650 °C, $\text{Na}_6\text{Al}_4\text{Si}_4\text{O}_{17}$ was formed. In the mixture with an $\text{Al}_2\text{O}_3$ excess, $\text{Na}_8\text{Al}_4\text{Si}_4\text{O}_{18}$ was also detected. The zeolitization of sodium aluminosilicates and unreacted metakaolin during hydrothermal crystallization in the NaOH solution with concentration of 2 mol l$^{-1}$ allowed synthesizing the LTA zeolite (Fig. 1).

The pellets from the stoichiometric mixture contained 91 wt% zeolite and the remainder was unreacted $\text{Na}_6\text{Al}_4\text{Si}_4\text{O}_{17}$ and other byproducts. The pellets from the mixture with an $\text{Al}_2\text{O}_3$ excess contained 97 wt% LTA.

Acknowledgements

The study was funded by RFBR according to the research project No. 16-03-00163 A.
SORBENT PREPARATION BY CO-GRINDING POWDER COMPOSITION
OF Z/CaO/Al(OH)₃ (Z = ZnO OR Zn₄CO₃(OH)₆)

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The co-grinding processes for ZnO/CaO/Al(OH)₃ and Zn₄CO₃(OH)₆/CaO/Al(OH)₃ powder compositions in a vibratory mill with an impact-shear loading were studied. The solid phase was investigated by the methods of X-ray diffraction, IR spectroscopy, scanning electron microscopy, synchronous thermal analysis and other methods. It was found that the formation of new Ca(Zn₂(OH)₆) phase takes place only in the ZnO-containing mixtures. The detected calcium hexahydroxodizincate dehydrate crystals had a prismatic shape. The experimental data showed also that the co-activation process is accompanied by the hydration of the particle surface due to the alignment of the basic properties of the initial compositions. The amount of gibbsite in the composition influences the changes in a crystal structure. The co-grinding of both composition allows one to obtain the pellets which keep the mechanical durability after the saturation with HCl vapors (Table).

Characterization of the sorbents

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molar ratio ZnO:CaO:Al₂O₃</th>
<th>Grinding time, min</th>
<th>Mechanical strength of pellets, MPa</th>
<th>Parametrs of a sorbent on it being kept over an HCl solution (Pₜₜₜ = 4.4×10⁻⁵ mm Hg)</th>
<th>gain in mass, %</th>
<th>Cl⁻ content, mg·g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/CaO/Al(OH)₃ 1:1:1</td>
<td>0</td>
<td>&lt; 0.5</td>
<td>Destroyed</td>
<td>mechanical strength of pellets, MPa</td>
<td>3.63±0.05</td>
<td>0.30±0.02</td>
</tr>
<tr>
<td>10</td>
<td>3.7±0.3</td>
<td>1.8±0.2</td>
<td>4.25±0.07</td>
<td>0.21±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO/CaO/Al(OH)₃ 1:1:2</td>
<td>0</td>
<td>&lt; 0.5</td>
<td>Destroyed</td>
<td>3.54±0.06</td>
<td>0.17±0.01</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3.4</td>
<td>2.0±0.2</td>
<td>4.16±0.07</td>
<td>0.18±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn₄CO₃(OH)₆/CaO/Al(OH)₃ 1:1:1</td>
<td>0</td>
<td>&lt; 0.5</td>
<td>Destroyed</td>
<td>6.94±0.06</td>
<td>0.50±0.02</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.3±0.2</td>
<td>2.2±0.3</td>
<td>10.9±0.07</td>
<td>0.34±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn₄CO₃(OH)₆/CaO/Al(OH)₃ 1:1:2</td>
<td>0</td>
<td>&lt; 0.5</td>
<td>Destroyed</td>
<td>7.05±0.05</td>
<td>0.38±0.01</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3.2</td>
<td>3.2±0.3</td>
<td>7.19±0.06</td>
<td>0.29±0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It was shown that the compositions with the basic zinc carbonate are characterized by the higher absorption capacity for the HCl vapors.

Acknowledgements

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SYNTHESIS AND INVESTIGATION OF UNSATURATED COBALT MONOCARBOXYLATE AND PRODUCTS OF ITS THERMOLYSIS

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Cobalt (II) carboxylates of unsaturated monocarboxylic acids (MCA), such as acrylic, crotonic, linoleic, methacrylic, oleic, sorbic and pentynoic acids, are synthesized; thermolysis of synthesized carboxylates was carried out and obtained nanocomposites were studied by methods of transmission and scanning electron microscopy, and X-ray diffraction (XRD).

Syntheses were carried out from aqueous solutions, except for cobalt oleate. Acid sample was dissolved in water and the cobalt carbonate monohydrate (CoCO$_3$·H$_2$O) sample was added until the end of carbon dioxide generation. Synthesis was carried out by preparing an aqueous solution of sodium linoleate, followed by the adding the sample of cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O), in case of linoleic acid. Cobalt oleate was synthesized for three hours at 70°C under reflux from the mixture of hexane-ethanol-water. Wherein previously the oleic acid was saponified, followed by addition of cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O) sample. These carboxylates were characterized by thermal, elemental and titrimetric analyses and IR spectroscopy.

All synthesized cobalt carboxylates (II) are salts with composition: Co(RCOO)$_2$·xH$_2$O. Acrylate carboxylate contains one molecule of water; crotonate, methacrylate and pentinate carboxylates contain two molecules of water; sorbate one contains four molecules of water; linolate and oleate ones contain eight molecules of water.

Nanocomposite were obtained as result of thermal decomposition of carboxylates under argon atmosphere at 335°C for 9 hours.

These nanocomposites (Fig. 1) consist of CoO+Co phases and polymer one by results of X-ray diffraction (XRD). Nanoparticles of CoO (cubic system, the lattice parameter $a = 4,257$ Å) and minor impurities of metallic cobalt ($\beta$-Co) (cubic system with lattice parameter $a = 3,536$ Å) are implemented in organic polymer matrix.

Calculated Enthalpy of formation reaction of cobalt (II) carboxylates ($\Delta H^\circ$) was calculated with semi-empirical quantum-chemical method (PM3) by using the software product (SP) HyperChem 8.0.8 (Hypercube Inc.).

The nanoparticle size distribution and its average diameter ($d_{av}$) for thermolysis products of cobalt (II) pentinate and crotonate by using SPLabview 8.5.1 for automatic photo processing were determined.

Linear positive correlation between the average diameter of the nanoparticles ($d_{av}$) and the enthalpy of formation reaction of unsaturated cobalt (II) monocarboxylates ($\Delta H^\circ$) was defined.

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SODIUM FLUOROSILICATE PROCESSING

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At present production of fluorine-containing compounds is developing quite rapidly. Apatite is the mineral, which possesses industrial value. As a result of apatite concentrate annual processing (~15 million tonnes per year) it is possible to get about 70 thousand tonnes of rare earth elements oxides as well as 200 thousand tonnes of strontium oxide and 250 thousand tonnes of fluorine [1]. Nitric-acid processing of apatite presumes apatite decomposition with subsequent calcium nitrate release. Afterwards fluorine being a waste product releases in form of sodium hexafluorosilicate \((\text{Na}_2\text{SiF}_6)\). Therefore, the issue of a current study is to develop a technique of sodium hexafluorosilicate processing with subsequent fluoride compound recovery.

Sadykova et al. investigated a number of chemical reactions devoted to \([\text{SiF}_6]^{2-}\) decomposition leading to simple fluorides and silicates obtainment. \(\text{Na}_2\text{CO}_3\), \(\text{K}_2\text{CO}_3\), \(\text{NH}_4\text{OH}\) were chosen for apatite decomposition.

The study of \(\text{Na}_2\text{SiF}_6\) and \(\text{Na}_2\text{CO}_3\) interaction result in \(\text{NaF}\), \(\text{SiO}_2\cdot\text{nH}_2\text{O}\) and \(\text{CO}_2\) derivation as reaction products. Silicic acid from resulting sediment was removed by washing with alkali solution. \(\text{NaOH}\) solution was chosen due to its property to form soluble \(\text{Na}_2\text{SiO}_3\) as a result of its interaction with silicic acid. \(\text{Na}_2\text{SiO}_3\) is easily separated from sodium fluoride sediment.

\(\text{Na}_2\text{CO}_3\) to \(\text{K}_2\text{CO}_3\) replacement in similar conditions leads to formation of both \(\text{NaF}\) and intermediate product \(\text{K}_2\text{SiF}_6\). Resulting sediment re-treatment with \(\text{K}_2\text{CO}_3\) solution leads to \(\text{KF}\) and \(\text{SiO}_2\cdot\text{nH}_2\text{O}\) formation. \(\text{SiO}_2\cdot\text{nH}_2\text{O}\) was removed by washing with alkali solutions in the case of \(\text{Na}_2\text{CO}_3\). Therefore \(\text{Na}_2\text{SiF}_6\) application as decomposition agent requires an excess of \(\text{K}_2\text{CO}_3\). The result product is mixture of \(\text{NaF}\) and \(\text{KF}\), their separation is due to the difference in their solubility.

\(\text{NH}_4\text{OH}\) and \(\text{Na}_2\text{SiF}_6\) interaction leads to - sodium fluoride and \(\text{SiO}_2\cdot\text{nH}_2\text{O}\) precipitation. After precipitate treatment with alkali solution, the X-ray pattern of investigated sample reveals the only sodium fluoride reflexes. Aqueous phase contains ammonium fluoride and silicic acid as reaction products. Aqueous phase vaporization followed by precipitate treatment with sodium hydroxide leads to \(\text{NH}_4\text{F}\) release and its purification out of \(\text{SiO}_2\cdot\text{nH}_2\text{O}\).

Finally, \(\text{NaF}\), \(\text{KF}\) and \(\text{NH}_4\text{F}\) were established to be the resulting products of interaction between \(\text{Na}_2\text{SiF}_6\) and involved compounds. The resulting products were isolated in solid form and then purified from impurities \(\text{SiO}_2\cdot\text{nH}_2\text{O}\). \(\text{NaF}\), \(\text{KF}\) and \(\text{NH}_4\text{F}\) are commercially useful products. Besides, these compounds can serve as fluorinating agents in rare earth fluorides production of.

Corresponding results were obtained in the framework of state task of the Ministry of Education and Science of Russia.

Reference:

Rapid development of semiconductor photoelectronics are a necessary condition for intensive development of the devices registration infrared (IR) radiation production which are used in a variety of civilian applications areas, such as medicine, transportation, construction, environmental monitoring, flight control and navigation systems.

Topical development direction of IR technology is to increase the number of sensitive elements of the detector and to transit from multi-row scanned systems to large-format beholder-type photodetector, in which each pixel corresponds to a photosensitive member. On this basis, the photosensitive material should have a high uniformity of composition distribution, a high structural perfection and suitable for instrumentation applications surface quality. The growing epitaxial techniques most fully satisfy these requirements. The aim of our work is to study the process of indium antimonide growing epitaxial layers (EL) on heavily doped n + -InSb substrates by liquid-phase epitaxy (LPE) suitable for matrix photodetectors producing with the spectral sensitivity range 3-5 microns.

The technological processes and management processes representation is one of the effective management of the conditions for obtaining EL with desired properties. It should be formalized, concise, easy to grasp and to analyze. Standardized in the Russian Federation the methodology for functional modeling (FM) is one of the modern methods of formalized description of processes. The use of this methodology for the joint description of the technological processes and management processes has been suggested. Conducting FM with sequential decomposition of individual processes allows to clearly regulate the performed actions, the used materials and their requirements, the technological equipment, and the choice of control parameters.

FM of the control of growing epitaxial layers of InSb LPE process requires consistent implementation of the following stages: verbal description of technological processes; establishment of relationships between the properties of epitaxial layers of InSb and conditions of their synthesis and detection of control parameters; sequential decomposition "from general to specific" technological processes and management processes.

Control of the samples is carried out following procedures: determination of photoconductivity relaxation time of minority carriers in the epitaxial layers of InSb; determination of majority carrier concentration in the epitaxial layer of the n-n-n + structures based on InSb; determination of electrons concentration in the InSb substrate and determination of the InSb EL thickness on the reflection spectra and the sample bandwidth. The functional diagram shows the preparation stages of raw materials, the main stages of the LPE, control methods EL obtained and obtained properties dependence on the conditions of the LPE.

Thus, the development of a management functional model of the InSb EL growing process on heavily doped n + -InSb substrates by LPE provides a clear and formalized description of processes, analysis of quality management procedures and processes.

The resulting model is a step in providing information support of InSb EL growing process.
INVESTIGATION OF EXPANDED GRAPHITE SYNTHESIS

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In the recent years, the research area of creating the new carbon materials for novel applications was developed. Graphite materials have great potential for their use in industry. One of such materials is thermally expanded graphite (TEG). The area of its application is very wide: petrochemical industry, nanotechnology, electronics and automotive industry etc. TEG is synthesized by chemical or thermal treatment of intercalated graphite or graphite oxide [1, 2]. The advantage of this material in a comparison with other graphite-like materials is high specific surface area, thus it can be used as a sorbent, catalyst support and as filler in polymer composites [3] etc.

The aim of this study was to investigate the role of synthesis parameters in the formation of TEG properties. In this study, the intercalated graphite (brand EG-350-50, Chemical Systems Co.) was used to obtain TEG. TEG can be prepared from intercalated graphite by two different approaches. The first is thermal shock: the method represents the heating of the sample with extremely high rates (500-1000 °C/sec). The second approach, which was used in this study, is the “dynamic” heating. The sample is heated using relatively low heating rate (10-20 °C/min) to relatively moderate temperatures (400-600 °C). This method has much broader potential for engineering the TEG properties and characteristics.

In this work, thermal expansion program consisted of two main steps and include various cooling techniques. The first step – the heating, beginning at room temperature (25 °C) to final temperature (400 °C, 500 °C, 600 °C, 700 °C) using the rate of 20 °C/min. The second step is the sample cooling, which was carried out in two ways (in the oven – first method of cooling; in the air – second method of cooling). Bulk density, TEG yield, specific surface area of TEG, obtained by these techniques, were analyzed.

According to the results obtained, it can be mentioned, that the first method allowed to achieve the high TEG yield and specific surface area. In conclusion, it is worth noting that the optimization of TEG synthesis will allow synthesizing material the advanced properties using flexible conditions that can be improved significantly by the use of method, proposed above.

Acknowledgements

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References:


INTEGRATED RECYCLING OF MANGANESE ORE

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The recycling of carbonate ores is a prospect for both valuable raw materials and solution of environmental problems. One of such places - Midnight manganese deposit. Midnight ore deposit extends for 1,500 meters from south to north, with a width of 600 meters. In the primary carbonate deposits of Midnight ores average content of compounds is following: manganese – 20.7%, iron – 3.6% and phosphorus – 0.19%. The oxidized ores has higher content of manganese – an average of 27.5% what is of great interest for its recycling.

Previously dried manganese ore from Midnight deposit has been taken to investigate (ore moisture content – 20%). The chemical composition of the dried raw materials is shown in a Table.

<table>
<thead>
<tr>
<th>Compounds, %</th>
<th>MnO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>ZnO</th>
<th>BaO</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese ore</td>
<td>67.17</td>
<td>3.08</td>
<td>0.54</td>
<td>11.74</td>
<td>12.41</td>
<td>2.81</td>
<td>0.68</td>
<td>0.435</td>
<td>1.03</td>
<td></td>
</tr>
</tbody>
</table>

*LOI - Loss on Ignition

Samples of the manganese ore have been ground to a size less than 0.315 mm. Leaching has been carried out with a solution of hydrochloric acid (35% with excess of stoichiometry 10%) and 25% solution of ammonium hydrogensulfate. Leaching time is 30 minutes at the temperature of 80 °C with constant stirring of 60 – 120 rpm. Obtained leach slurry has been filtered, washed and dried. The resulting acid-balance is of 33% and it has been reserved for research in order to explore the possibility of producing ceramic materials (SiO₂ = 30.73%).

Optimal deposition conditions have been determined to the filtrate FeCl₃ + 3NH₄OH = Fe(OH)₃↓ + 3NH₄Cl. Concentration of the ammonia solution is 10%. Ammonia solution has been poured into the chloride solution under stirring 120 rpm. The temperature is of 60 °C. The final pH of precipitation is of 5.5-6.0. Having precipitated sludge has a complete rest in bed for 10 minutes. Obtained iron hydroxide (III) has been left to research to obtain iron oxide-binder for agglomerating of iron ores and to develop technologies for obtaining the iron-oxide pigments.

Optimal conditions for deposition of manganese carbonate have been determined as well, MnSO₄ + (NH₄)₂CO₃ = MnCO₃↓ + 2NH₄SO₄. The concentration of ammonium carbonate solution is 30%, ammonia is of with excess of stoichiometry 10%. Ammonia solution has been poured into the chloride solution under stirring 30 rpm. The temperature is of 20 – 40 °C. The final precipitation pH is 9.0. The sediment has been matured for 30 minutes. The mixture of manganese carbonate and calcium carbonate obtained from ore has been calcined at 300 °C and manganese oxide (IV) has been obtained.

\[ \text{MnCO}_3 = \text{MnO} + \text{CO}_2 \uparrow (200^0 \text{C}); \]
\[ 2\text{MnO} + \text{O}_2 = 2\text{MnO}_2 (300^0 \text{C}) \]

Conclusions:

1. We have proved the technological possibility of hydrometallurgical recycling of Midnight ores having got the three finished products.
2. We have determined the optimum parameters of technological operations.
3. Samples of manganese high-quality raw materials have been obtained at which replacement of imported raw materials is possible (MnO₂ = 92%; CaO = 5.44%).
INVESTIGATION OF THE PROPERTIES OF A MAGNESIUM SUBSTITUTED HYDROXYAPATITE

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During the synthesis of composite materials (CM) based on the magnesium-substituted calcium hydroxyapatite (MHA) from aqueous solutions developed a method for the directed synthesis of biocompatible materials.

Evaluation of the effect of magnesium ions on the characteristics of HA with physico-chemical analysis methods (chemical, XRD, IR, TDG, SEM, TEM) assessed the influence of the synthesis conditions and the composition of the CM on the size and morphology of the HA crystals.

Under in vitro conditions the solubility HA-CM and analyzed the possible consequences of interaction between magnesium and CM to the native tissue were analyzed.

Hydroxyapatite is the major inorganic component of the native bone.

Due to its high biocompatibility and bioactivity HA is widely used in medicine as an implant material.

Native apatite tissues of mammals are the main components (~ 60%) of bone and dental tissues and are nanoscale (~ 5-50 nm) needle-shaped crystals habit with cationic and anionic substitutions in the HA crystal structure.

Stoichiometric crystalline HA is an inorganic crystal-analogue component of mineralized tissues of mammals and serves as a model object for studying the influence of various factors on the physico-chemical, medical and biological characteristics of the inorganic components of bone and dental tissues. In the synthesis of partially substituted hydroxyapatite specifically introduced into its structure certain ions, either to charge compensation or adjustment for physico-chemical properties (such as solubility).

Thus, the problem of isomorphic substitutions in hydroxylapatite is very important. Magnesium choice due to its important role in physiological processes.

During the obtained results differing scientific novelty and practical importance, including: development of methods for the directed synthesis of new materials for medical use as implants with controlled physical-chemical, medical and biological characteristics; evaluation of the effect of natural metabolites of bone (magnesium) on the solubility characteristics of HA in model experiment. It is proved that MHA exhibits a high biocompatibility and bioactivity.
METHODS OF DIRECTED FUNCTIONALIZATION OF CLOSO-DECABORATE ANION SULFANYL DERIVATIVE

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Over decades of studying closo-decaboron anion \([B_{10}H_{10}]^{2-}\) from the moment of its revealing, a lot of derivations with exo-polyedrical functional groups have been obtained, such as (hydroxyl, acetyl, oxonium, halide, azid-, carbonyl-, nitro, amino, isonitrile [1–4]). At the same time sulfur containing derivations of closo-boron anions \([BnHn]^{2-}\) (n=1, 2) have always been of great importance to scientists [5]. First of all that is related to the successful use of sodium salt sulfonil derivation of dodecaboron anion \(Na_2[B_{12}H_{11}SH]\) (BSH) in curing malignant brain tumors.

In this work a new, effective and easy-to-do method of obtaining sulfanyl derivation of closo-decaboron anion \([2-B_{10}H_{10}SH]^{2-}\) from (undekahidro-closo-dekaboron anion \([B_{10}H_{11}]^-\)) was introduced [6].

The reactions of alkylation of \([2-B_{10}H_{10}SH]^{2-}\) derivation with various classes of compounds (Allylbromide, ethyl bromoacetate, iodoacetamide, butyl bromide, benzyl chloride, etc.) and acylation with acetylchloride and benzoylchloride were researched.

Compounds were described by NMR, IR spectroscopy and mass-spectroscopy. Structures of some compounds were confirmed by X-ray diffraction.

Acknowledgements

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References:

During the treatment of the aluminum raw material by hydrochloric acid method an aluminum chloride solution obtained, including aluminum hydroxychloride - coagulants for the purification of drinking water and wastewater. Physicochemical properties (such as density, viscosity, degree of polymerization, and others) of aluminum chloride solutions have been studied.

At the interaction of aluminum constituting the aluminum raw materials with hydrochloric acid takes place several successively proceeding stages: hydrochloric acid reacts with the aluminum to form aluminum chloride; aluminum chloride and the aluminum reacts with water to form low-base compound and then middle and high base aluminum hydroxychloride. Various ratio of Al:Cl in solution gives a different basicity of aluminum chloride solutions. Below are equations (1-3) of reactions for each of the modules basicity:

\[
\begin{align*}
\text{1/3} & \quad \text{Al} + 2 \text{AlCl}_3 + 3 \text{H}_2\text{O} = 3 \text{Al(OH)Cl}_2 + 1,5 \text{H}_2; \\
\text{2/3} & \quad \text{Al} + \text{Al(OH)Cl}_2 + 3 \text{H}_2\text{O} = 2 \text{Al(OH)}_2\text{Cl} + 1,5 \text{H}_2; \\
\text{5/6} & \quad \text{Al} + \text{Al(OH)}_2\text{Cl} + 3 \text{H}_2\text{O} = \text{Al}_2(\text{OH})_5\text{Cl} + 1,5 \text{H}_2.
\end{align*}
\]

In practice, also obtained of aluminiumhydroxo chloride with mixed modules basicity 1/3 + AlCl₃; 1/3 + 2/3 or 2/3 + 5/6 in a wide range of percentages.

Ratio of basic module with different parameters characterizing the shape of the aluminum hydroxychloride is presented in a Table.

The ratio of the various parameters in aluminium chloride solutions

<table>
<thead>
<tr>
<th>Composition</th>
<th>Basicity Modules</th>
<th>Modulus of acidity HCl/ Al₂O₃</th>
<th>Al/Cl ratio</th>
<th>Basicity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>–</td>
<td>6</td>
<td>0,33</td>
<td>–</td>
</tr>
<tr>
<td>Al(OH)Cl₂</td>
<td>1/3</td>
<td>4</td>
<td>0,5</td>
<td>33</td>
</tr>
<tr>
<td>Al(OH)₂Cl</td>
<td>2/3</td>
<td>2</td>
<td>1</td>
<td>66</td>
</tr>
<tr>
<td>Al₂(OH)₅Cl</td>
<td>5/6</td>
<td>1</td>
<td>2</td>
<td>83,3</td>
</tr>
</tbody>
</table>

As a result of our studies of physicochemical properties of aluminum hydroxychlorides was found that with increasing of temperature between 0 and 90°C, the viscosity decreases from 1 to 25 mPa, and with increasing of Al₂O₃ concentration from 7 to 21% by weight viscosity increases. Similar results were obtained by density of coagulants. In order to determine what type of hydroxocomplexes (monomers, oligomers or polymers) are produced in aluminum hydroxychlorides solutions of varying basicity depending on conditions of the synthesis was determined by their degree of polymerization. As a result, it was found that aluminum in low base aluminiumhydroxochloride represented mainly as monomer, middle base solutions by 58 wt. % composed of it too, high base contain less than 30% of the monomers, i.e. aluminum in it is preferably in the form of polymeric hydroxy complexes.
The Russian aluminum industry has experienced a shortage of high-quality raw materials from the moment it was created. Until recently, companies in the industry have been oriented toward the processing of bauxites with a high silica modulus ($\mu_S > 7$), and the deposits of these bauxites are located in Australia, South America, and Africa. The importation of raw materials (bauxites and alumina) is now becoming less profitable due to increases in transportation costs and the incipient worldwide shortage of high-quality bauxites. At the same time, Russia does possess enormous reserves of low-grade aluminum ores that have not traditionally been used by the aluminum industry. Among these resources are high-silicon bauxites, kaolins, coal fly ash formed at heat and power plants, and anorthosites. The anorthosite reserves are estimated to be hundreds of millions of tons and can serve as an effective raw-materials base. Studies of the processing of such ores are very important and are actively being pursued in Canada, China, and other countries with an established aluminum industry. Until recently, the main obstacle to further progress in the use of acid-based technologies for obtaining alumina has been the lack of reliable and productive equipment that is resistant to acids. With the advent of new materials and processing methods, equipment which is suited for acid-based (including hydrochloric-acid-based) hydrometallurgical technologies has now become readily available. Extensive reserves of low-grade ores in Siberia have been discovered and large electrolysis plants have been built near them. These developments give reason to hope that the industrial-scale production of alumina by hydrochloric-acid-based technology will commence in the near future.

In this research was found that, in the case of autoclave leaching of bauxite by hydrochloric acid, the aluminum extraction rate in the solution reaches 94–98%. Mechanism for bauxite dissolution in hydrochloric acid was proposed. It was shown, that the process rate is limited by the kaolinite dissolution as the most resistant mineral. The process takes place in steps in three stages: at temperatures of 150–160°C in the kinetic region ($E_a = 70.22$ kJ/mol, $n = 0.52–0.61$), at 160–170°C in the transition region ($E_a = 40.88$ kJ/mol) and at 170–180°C in the diffusion region ($E_a = 22.66$ kJ/mol, $n = 0.92–1.09$). X-Ray phase analysis and Scanning electron microscopy showed that the surface of bauxite particles is covered by hard films of silica. These films block the diffusion of hydrochloric acid to the reaction zone, which reduces dissolution rate and the amount of aluminum recovered in the solution.

Separation of aluminium and iron chlorides after autoclave leaching bauxites in hydrochloric acid by salting out method are investigated. The conditions influencing on the content of main impurity in $\text{AlCl}_3\cdot6\text{H}_2\text{O}$ are studied.

Conducted physico-chemical study of the roasting process $\text{AlCl}_3\cdot6\text{H}_2\text{O}$ and the main peaks of the removal of water and Cl-ion. It is shown, that the chlorine-ion is mainly excreted in the form of HCl. The influence of roasting temperature on the phase composition and basic physical properties of powder of aluminium oxide (specific surface, porosity, average particle size) depending on the calcinations temperature were investigated. The results of optical and electron microscopy show, that particles of alumina retain the original hexagonal structure of $\text{AlCl}_3\cdot6\text{H}_2\text{O}$. The effect of ultrasonic treatment on dispersibility of powder of alumina oxide was researched. The obtained data allows to obtain sandy grade alumina, which can be used to produce aluminum metal in the electrolysis process.

**Acknowledgements:** This work was supported by Department of Chemistry and Materials Science of the Russian Academy of Sciences № IV.5.6 in 2016.
Electrochemical methods of definition of inorganic substances find wide application in science and industry and actively develop. One of such methods is the voltamperometry. In the majority of voltamperometric techniques of analysis the mercury electrode is used, but metal mercury is poisonous and inconvenient in use. The purpose of the work was the development of a solid-state electrode with similar properties to a mercury electrode.

The platinum ultramicroelectrode, which consists of 8 wires with a diameter of 20 microns, sealed into a glass tube, has been taken as a basis. It is worth noting its unique properties: spherical diffusion, small values of current, an opportunity to work in environments with various conductivity, lack of formation of the gas bubbles and crystals of substance on his surface because of his small size.

Stages of creation of the electrode (Table 1) as the result of which the platinum ultramicroelectrode with double modification has been received: electrochemical cleaning, electrochemical accumulation of a copper layer, electrochemical accumulation of a mercury film.

The voltamperogram in the direct current mode was obtained in order to evaluate the application of a copper layer qualitatively in solution of 0,1 M of NaOH. This voltamperogram coincided with the voltamperogram of a copper electrode.

The developed electrode has been used for definition of aldehydes and ketones by the method of indirect polarographic recovery. This technique is well-known, the mechanism of definition is studied. In this work the definition of formaldehyde, ethyl aldehyde and benzole aldehyde has been carried out. The received results are given in Table 2.

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Half-wavepotential, mV</th>
<th>The detection limit, mol/L</th>
<th>Limit of detection, mol/L</th>
<th>Dispersion</th>
<th>MPCw, mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>-1275</td>
<td>6*10^{-8}</td>
<td>3*10^{-6}</td>
<td>0,36</td>
<td>2*10^{-6}</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>-1325</td>
<td>7*10^{-7}</td>
<td>1*10^{-6}</td>
<td>0,35</td>
<td>4,5*10^{-6}</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>-1025</td>
<td>1*10^{-8}</td>
<td>2*10^{-8}</td>
<td>0,30</td>
<td>3*10^{-8}</td>
</tr>
</tbody>
</table>
STABILITY COMPLEX COMPOSITION SOLUTIONS OF RARE EARTH ELEMENTS

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Complex composition solutions containing lanthanide cations together with silicate- and phosphate- anions, as well as traces of iron cations, aluminum, calcium, titanium, etc. [1] are formed by removing the rare earth elements (REE) in a phosphate-silicate ores. Solutions of this composition is extremely unstable in time, we tend to gel formation and precipitation, which complicates isolation of such rare earth solutions by precipitation or extraction. Results of stability study of solutions are given in this message in the system: Ln(NO3)3 - HNO3 - H3PO4 - NH4NO3 - 100% TBP, which are formed in particular in the processing of apatite. Precipitation in such solutions mentioned in the works of Moeseev S.D. et al. [2]. It is found, that increasing the concentration of NH4NO3 solution increases the resistance, but causes additional and very significant transition of nitric acid in the organic phase, which leads to the formation of deposits in the water phase, due to reaching PR. Increasing concentrations of HNO3 solutions increases resistance, but reduces the distribution coefficient of REE. It is important to coordinate increase in nitric acid concentration in the organic phase, when the concentration of lanthanide nitrate and the salting-out agent in the aqueous phase. It is known, that nitric acid extraction isotherm changes significantly with increasing salting-out agent concentration in the aqueous phase. TBP supplied to the countercurrent cascade proposed nitric acid to saturate content of at least greater, than the concentration of nitric acid in the organic phase of the cascade of the cell, in which a raw aqueous solution:

\[ C_0HNO_3 = C_1HNO_3 + C_{aq} \]  

where: \( C_0HNO_3 \) - nitric acid content in the inlet to stage the organic phase, \( C_1HNO_3 \) - content of nitric acid in the entry chamber starting solution, \( C_{aq} \) - minimum concentration of nitric acid in the aqueous phase, which still do not fall precipitation and solution stable. It is found, that precipitation hydroxophosphate REE are formed in the aqueous phase, if not adhere to these guidelines. It is found that precipitation hydroxonitrate REE are formed in the aqueous phase, if not adhere to these guidelines. Equilibrium systems: Er(NO3)3 - NH4OH - NH4NO3; Dy(NO3)3 - NH4OH - NH4NO3 studied by conductometric titration, and found that at high concentrations of rare earth nitrate and ammonium nitrate are formed are stable at pH 6.5-7.0 hydroxonitrate REE solutions. Thus, the introduction of ammonium nitrate produces stable solutions at higher pH values exceeding pH REE several precipitation (i.e. to stabilize the solution), and presaturation TBP nitric acid to a value corresponding to equation (1), the extraction process to stabilize.

References:
SYNTHESIS AND INVESTIGATION OF PLATINUM METALNANOPARTICLES ON POROUS SILICON SUBSTRATES

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The preparation of nanoparticles is one of the most topical directions in modern materials science. Unique physical and chemical properties of nanoparticles make efficient catalysts for use in fuel cells (FC). A fuel cell consists of two electrodes containing catalytic layer separated by proton exchange membrane. The catalyst layer in FC is important factor, which is considerably influences on FC performance and which is determine the basic production costs of fuel cells.In both the anode and cathode, the catalyst layer is the location of the half-cell reaction infuel cell [1–3].

The aim of our research was the creation of new structural material, which is possessed higher functional and catalytic parameters. Porous silicon (PS) was effectively used as a functional matrix-support for nanocomposites formation. PS application allows to prevent catalyst agglomeration in current sources based on hydrogen-containing fuel oxidation. The application of bimetallic platinum metal nanoparticles allow to improve power source specific characteristics and increase the resistance to catalyst poisoning. Using the proposed novel method of synthesis in reverse micelles solution it was obtained nanoparticles with controlled sizeand shape [1, 2]. In order to select optimal conditions fornanoparticles synthesis: the solubilization degree (ω), platinum metals ratio in solution and concentration, porous silicon porosity degree, pore sizes and shape – it was carried out a wide range of research.

By varying the synthesis conditions one can control the nanoparticles size, content and emerging properties. By means of the electron microscopy, phase analysis, cyclic voltammetry methods it was performed the investigation of nanocomposite functional properties. It was found that the highest electrocatalytic activity have composites obtained from reverse micelle solutions with the solubilization degree of 5 based on silicon wafers with a porosity degree of 64%. According to the electron microscopy data, the nanoparticles were fixed not only on the surface but also in the volume of the porous silicon, the average size of nanoparticles was 1.5-1.9 nm for n- and p-type [2]. The obtained nanocomposites on porous silicon containing platinum metal nanoparticles of different composition, size and shape, can be used as functional membrane-electrode materials for micro-power energy converters.

Acknowledgements
The work was financially supported by the Russian Foundation for Basic Research (project № 15-03-05037-a).

References:
THE CREATION OF ELECTRODE MATERIAL WITH HIGH CATALYTIC ACTIVITY FOR FUEL CELLS BASED ON POROUS SILICON

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Improvement of catalytic characteristics of the electrode material in fuel cells is a necessary factor for the hydrogen energy development. In particular, the electrode material contributes to the cost of the fuel cell. Therefore, the improved catalytic abilities of the electrode material makes fuel cells more affordable [1–4].

To achieve this goal in our work it was used a porous silicon as a functional substrate. Porous silicon has several advantages over the traditional carbon substrates: high chemical and physical resistance, a large surface area of the pores and is easily integrated into the electronics. At present work nanocomposites based on porous silicon with bimetallic Pt-Pd nanoparticles (the metals ratio 1:1) were synthesized. Nanocomposites were investigated by means of electron microscopy and cyclic voltammetry (CVA).

The increase in catalytic abilities of the material produced by impregnating a porous matrix of silicon-solution with platinum nanoparticles. Production of porous silicon n- and p-type was carried out using electrochemical etching of monocrystalline silicon. The average pore diameter was 20-40 nm and the depth was 1 µm. Pt-Pd nanoparticles were synthesized by chemical reduction of platinum metal ions in water-organic solutions with ultrasonic treatment using NaBH4 as reducing agent. By varying the synthesis conditions one can control the nanoparticles size, content and emerging properties. By means of the electron microscopy, phase analysis, cyclic voltammetry methods it was performed the investigation of nanocomposite functional properties [1–3].

By electron microscopy it was revealed that the average size of the nanoparticles ranged from 8 nm or less. Preliminary tests of nanocomposites in model conditions of the fuel cell, using cyclic voltammetry (CVA) showed a high catalytic activity and stability of the obtained electrode materials in reaction of hydrogen oxidation and oxygen reduction [1, 2].

Acknowledgements
The work was financially supported by the Russian Foundation for Basic Research (project № 16-38-00862-mol_a).

References:
Section 5

Polymers and Polymer-Based Composites - Technological Principles and Methods of Synthesis, Modifying and Processing
SORPTION OF METAL IONS ON N-(2-SULFOETHYL) POLYAMINOSTYRENE WITH DEGREE OF MODIFICATION 0.7

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Currently for various analytical purposes polymeric complexing sorbents are widely used. One of the most important factors determining the selective properties of such materials is the degree of modification. Previously we showed that N-(2-sulfoethyl) polyaminostyrene-based sorbents with DS up to 0.6 selectively removed copper(II) and silver(I) ions from solutions of complex composition [1]. The present work is a continuation of studies on the selective properties of N-(2-sulfoethyl) polyaminostyrene with the highest degree of modification – 0.7. (NSE-polyaminostyrene with DS = 0.7).

Sorbent is synthesized in the Institute of Organic synthesis Ural Branch of RAS by polymer-analogous transformations of polystyrene [1].

In the present work the dependence of the sorption of metal ions at their collective presence by NSE-polyaminostyrene with DS = 0.7 from the pH of ammonium acetate buffer solution were investigated. Concentration of the metal ions in the solutions was determined before and after sorption by inductively coupled plasma atomic emission spectroscopy using a Thermo Scientific iCAP 6500 spectrometer. Obtained dependence is presented at Fig. 1.

![Fig. 1. Influence of acidity of medium on sorption of metal ions on N-2-sulfoethyl polyaminostyrene with DS = 0.7. Co-existence of metal ions in an ammonium acetate buffer solution. Initial CMe(II) = 1·10^{-4} mol/dm^3.](image)

Obtained curve shows that the studied materials have extracted selectively copper(II) and silver(I) ions from solutions of complex composition. Based on the data values of the coefficients of selectivity of silver(I) ions in comparison with copper(II) were calculated. The value of $K_{Ag(I)/Cu(II)}$ for sulfoethylated polyaminostyrene 0.7 at pH 6.5 amounted to 399.

Thus shown that of N-2-sulfoethylpoliaminostyrene with degrees of modification 0.7 is a promising material as has high selectivity for silver ions (I) and copper (II) and can be used to determine these ions in various objects.

Reference:
Heat-resistant structural polysulfone (PSU) have a high melt viscosity and are processed at high temperatures (over 300°C) by extrusion and injection molding. A rheological additive of different nature was added to PSU melt with the purpose to reduce of viscosity and to improve of processability. Selecting of the rheological additive is not a simple technological problem. Note that the rheological additive must not be highly soluble in the polymer and have sufficient thermal stability, does not degrade at the PSU processing temperatures.

In this paper, by the method of capillary viscometer (viscometer LCR 7000, Dynisco) have investigated the complex of rheological properties of PSU melt at different temperatures. The methodology was used that takes into account the effects of slippage during the flow of the melt to assess the effectiveness of the rheological additive. A special technique was used for research features of flow, including the sliding capillary wall characteristics of the compositions based on PSU with a rheological additive. It developed at the Moscow Institute of Technology (Campus MITHT) at the Department of Chemistry and technology of plastics and polymer composites.

It was shown that rheological additive no effect on the character of the flow while adding on the manufacturer recommendation an amount of up to ~ 1 mass %. It was not shown the effect of sliding of melt on capillary wall. Possibly, fluorine rheological additive dissolves in the melt PPS at high processing temperatures (290 to 320°C), which reduces the efficiency of its action as a lubricant.

It is recommended to increase the content of the rheological additives and reduce its solubility for achievement slip effect and improve processability of PSU.
STUDYING OF OXIDIZING PROPERTIES OF RUBBER MIXES STABILIZED BY OLIGOMER ANTIOXIDANTS

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From literary data it is known that efficiency of effect of many antioxidants in processes of oxidizing destruction of polymers and including rubbers decides by ease of a separation of atom of hydrogen of hydroxyl group and ability to interaction on free radicals with formation of stable products of reaction. Anti-oxidizing activity of stabilizers is connected with an inhibitor molecule structure. Now the most effective stabilizers is phenolic and naphtholic antioxidants.

Rubbers in the main SKI-3 it is widely used for production of tires and rubber products. These rubbers possesses high not limitation and substantially is exposed to aging. For preservation of structure and properties of SKI-3 rubber and its cured stock from oxidizing and other undesirable processes on his basis enter antioxidants including naphtholic type into composition of rubber mixes.

Was of interest to investigate influence of antioxidants on the basis of gossypol on kinetics of thermodestruction of SKI-3 rubber for the purpose of determination of kinetic parameters of his decomposition and specification of the mechanism of the inhibiting operation of stabilizers. Investigated oligomer antioxidants are synthesized on the basis of gossypol with organic compounds and are called as GAA, GATM, GEHG and EIDERS, and their studying as the thermostabilizer is of a certain practical interest to SKI-3 rubber.

Research of influence of antioxidants on process of thermooxidizing destruction of synthetic SKI-3 rubber was studied by methods of IK-spectroscopy and the differential and thermal analysis (DTA). The IR spectrums of films of SKI-3 rubber which are containing and not containing oligomer antioxidant on the basis of gossypol before aging (140 °C x 180 min.) are received.

Determined by method of infrared spectroscopy efficiency of antioxidants (by accumulation of carbonyl groups). Rubber for carrying out research was previously purified of industrial additives triple reprecipitation by ethanol from the toluene of solutions. Samples for oxidation were prepared by casting of films on a surface of plates from NaCl from 20% solutions of rubber in toluene. IR spectrums of films of rubbers were removed on a spectrometer of "Perkin-Elmer" with the Truck transformation.

By results of research it has been established that distinction in an arrangement the gossypol of deputies in relation to OH-group practically doesn't influence their anti-radical activity.

In a range of the oxidized rubber decrease in intensity of strips of absorpti on in 1470-1290, 900-690, 1310-1280, 1420, 1385-1370 cm⁻¹ corresponding to groups (–CH–), (–HC=CH–), (– CH₃) rather initial sample of rubber, indicates destruction of the main chains of SKI-3 rubber. In IR spectrum of the oxidized sample of the rubber containing GEHG, intensity of these strips of absorption increases that corresponds to bigger preservation of carbon-chain structure of rubber in the presence of the GEHG oligomer antioxidant.

From the carried-out data it is visible that in the presence of the GEHG oligomer antioxidant decrease in intensity of course of thermooxidizing processes, concerning a sample, in which not containing antioxidant is observed that promotes the best preservation of molecular structure of an elastomer.
INVESTIGATION OF THERMAL DEGRADATION OF EPOXY COMPOSITES BASED ON CARBON NANOMATERIALS

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Currently, epoxy resins (ER) are widely used in various fields of industry as a binder in the manufacturing of polymer composites, protective coatings, adhesives, impregnating material to create prepregs etc. However, there is one problem of these materials is their low thermooxidation stability. The influence of elevated temperature induces the strong degradation of ERs and this effect is very critical for their industrial applications. Addition of carbon nanomaterials to epoxy matrix makes these materials sustainable to high temperatures. Addition of carbon nanotubes and thermally expanded graphite increases the resistance of epoxy composites towards heating [1, 2].

It is worth noting that publications devoted to study of the thermal stability of epoxy composites based on these materials are presented incomplete data that prevent their industrial application. In this work, the thermal degradation of epoxy composites based on carbon nanomaterials (multi-walled carbon nanotubes, thermally expanded graphite) was investigated. The treatment of thermal analysis data for determination of composite degradation kinetics was carried out.

Two groups of samples were obtained: the first – with addition of multi-walled carbon nanotubes (MWNTs); the second – with addition of thermally expanded graphite (filler content up to 5 wt.%). There were two hardeners used for preparation the composites: PEPA and TETA. The samples obtained were examined by simultaneous thermal analysis (STA 449C NETZSCH).

Thermal degradation curves of composites obtained at different heating rates (5, 10 and 15 K/min) was measured by NETZCH Thermokinetics software. A kinetic analysis was performed using a model-independent methods for evaluating the kinetic parameters: Friedman method and Ozawa-Flynn-Wall, which made it possible to determine the number of process steps, the type of the reaction and the contribution of each stage in the process.

On the basis of data obtained it was determined that both carbon nanomaterials improved thermal degradation stability of epoxy composite. It should be noted that the MWNTs and thermally expanded graphite is a promising material for the use as filler in epoxy composites that are able to retard their oxidation. The data obtained will be used for determination of epoxy composite degradation kinetics.

Acknowledgements

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References:


NEW CURING AGENTS OF SILICONE RUBBER AND A METHOD FOR THEIR PREPARATION

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Previously, it was shown that the organosilicon compounds containing chlorine atom in carboposition react with amines to form derivatives of 2,5-disilapiperazine.

We have studied the interaction of triethoxychloromethylsilane with carbaminosilane (I, II) in the presence of trimethylamine (IV), which lead to obtaining of linear polyfunctional amines.

It has been established that [3-(triethoxysilyl)propyl]amine (I) reacts with triethoxychloromethylsilane (III) under mild conditions to form previously unknown polyfunctional amine – [(triethoxysilyl)methyl][3-(triethoxysilyl)propyl]amine (V):

\[
(C_2H_5O)_3Si(CH_2)NH_2 + ClCH_2Si(OH)_3 + Et_3N \rightarrow (C_2H_5O)_3Si(CH_2)NHCH_2Si(OH)_3 + Et_3N*HCl
\]

The reaction was carried out at a temperature of 65 °C for 12 hours without the use of a catalyst, the yield of product (V) was 91%.

The use of other carbaminosilane – N-[2-(aminoethyl)-N-3-(trimethoxysilyl)-propyl]amine (II) allowed to establish that in this case, the interaction with triethoxychloromethylsilane (III) takes place easily to form amine – N-[(triethoxysilyl)methyl]-N´-[3-(trimethoxysilyl)-propyl]ethane-1,2-diamine (VII) with the same yield:

\[
(CH_3O)_3Si(CH_2)NH(CH_2)NH_2 + ClCH_2Si(OH)_3 + Et_3N \rightarrow (CH_3O)_3Si(CH_2)NHCH_2NHCH_2Si(OH)_3 + Et_3N*HCl
\]

The process was carried out at a temperature of 65 °C, but for 33 hours.

The resulting polyfunctional amine (V and VII) have been successfully tested as a curing agents of silicone rubbers, with positive results.

Reference:
NEW COMPOSITE MEMBRANES FOR FUEL CELLS
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One of the most promising direction in the field of development new proton exchange membranes (PEM) for high-temperature fuel cells are aromatic polymers with functional groups which can effectively conduct protons at temperatures above 120 °C under anhydrous conditions and maintain the performance of at least 10000 operating hours. Outstanding successes were achieved using the system of polybenzimidazole-phosphoric acid (PBI/H₃PO₄) which maintain stability and conducting properties at temperatures above 300 °C. Among the disadvantages, there are low mechanical properties of PEM based on PBI/H₃PO₄, especially at high doping levels, furthermore membranes from polybenzimidazoles are rather expensive, due to the complexity of preparation of monomers. In this regard, a number of studies have been aimed at solving these problems through development of more efficient composite PEM by mixing PBI with inexpensive sulfonated polysulfones with further doping the resulting mixture. There is good mix of polymers due to the formation of hydrogen bonds between the NH - groups of PBI and sulfonic groups of polysulfones. The properties of such membranes depend on the ratio of PBI and polysulfone, sulfonation degree of the latter, the temperature and amount of doping agent.

Further to this work we have prepared new PEM, based on the mixture of the polybenzimidazole-type AB (6-Cl-PFOBI) and sulfonated poly(arylene ether sulfones) (sPAES), followed by phosphoric acid doping of cast films. Polymer synthesis schemes are shown below:

The structures of synthesized polymers were analyzed by FT-IR spectroscopy and elemental analysis. The thermo-mechanical characteristics of polymers with various mixing ratio were studied before and after the doping, experiments to establish the proton conductivity of obtained PEM were carried out.

Acknowledgements
The work was supported by President RF grant MK-3839.2015.3.
This article presents the results of experiments for the processing of industrial vegetable oils, which are triglycerides of unsaturated fatty acids containing mainly 18 carbon atoms. Significant difficulties in processing were associated with a high degree of contamination of the oils, which were used in the study. This circumstance has led to the need for development of the technology for processing of vegetable oils by the decomposition of triglycerides to the corresponding unsaturated fatty acids (FA) or their derivatives, as well as to glycerine with the corresponding impurities. Synthesis of the aliphatic esters of unsaturated fatty acids has been evaluated to be the most preferred result compared with the decomposition of the glycerides of industrial vegetable oils to the fatty acids themselves. In this method of processing it is possible to work with the fairly pure chemical substances, and further processes such as distillation, storing, transportation and processing of the esters proved to be more cost-effective and safe rather than the corresponding processes with the fatty acids. Currently, the main sources of fatty acids and their derivatives in Russia are linseed, castor, sunflower, cottonseed, soybean, coriander and other vegetable oils. Synthesis of intermediate products, which are to be used for the synthesis of non-toxic polymers and composite materials is possible by transfer of vegetable oils in their aliphatic esters, most often into methyl, ethyl or butyl esters. The next stage of processing is almost all known methods and techniques specific to the technology of basic organic and petrochemical synthesis - hydrolysis, esterification, hydration, alkylation, sulfation, nitration, oxidation, hydrogenation, dehydrogenation, etc. One of the perspective directions in the development of technology for non-toxic materials are works on creation of environmentally clean products from aliphatic high- and low-molecular poly- and oligoamides, which are used in the national industry as polymer and impregnating materials in the manufacturing of glass reinforced plastics, carbon fiber reinforced plastics, sealants and heat resistant protective rubber coatings and reinforced composites.

In this area the special interest and attention is to be paid to oligoaminoamides - low molecular weight polyamides obtained through the condensation of dimerized fatty acids of linseed (DFAL) and natural industrial oils with alkylenepolyamines. They have the unique properties: high adhesion, flame retardant, thermal stability and controlled depth of hardening. The country's lack of industrial production of dimer acids hinders the development of the process of obtaining composite materials on their basis. Therefore, the research on the determination of synthesis conditions of linseed oil dimerized fatty acids and implementation of the process in demo plant scale is a crucial task.

As a result of conducted experiments it was established that preliminary obtained (by the alcoholysis) aliphatic esters of vegetable oils unsaturated fatty acids can be subjected to thermal dimerization (temperatures from 280 to 320 °C, the duration of the process is from 10 to 15 hours) or to catalytic dimerization (temperature from 180 to 210 °C, the duration of the process is from 3 to 5 hours, the catalyst is the aluminosilicate zeolite catalyst for catalytic cracking in an amount of from 10 to 15 % (wt.) on the amount of fatty acids esters loaded into the process). The compounds formed can be used to produce non-toxic polyamides and composites with predetermined properties.
Butyl rubber (IIR) belongs to rubbers of a special purpose. It’s chemically inert, has low gas permeability, thermal stability and is widely applied in construction, rubber and light industries.

Artificial latexes of butyl rubber are of considerable interest, especially for dipping products. The process for artificial latex preparation consists of the following steps: obtaining a polymer solution in an organic solvent, it’s emulsification in an aqueous solution of surfactant, solvent stripping, the final product concentration.

Complexity of receiving the IIR artificial latexes is determined by need to select a surfactant capable to form the strong adsorptive layer on the surface of the polymer particles that keeps them from coagulation. There are no scientific approaches to the choice of a surfactant suitable for stabilization of artificial latex particles yet. Therefore it is necessary to make a complex research for their choice in each case.

In this work the task of producing the IIR artificial latex of 1675N mark with a positive charge of the polymer particles has been set.

These studies were started with the selection of the solvent and the nature of the surfactant. As solvents have been tested: tetrachlormethane, hexane, cyclohexane and toluene. Cyclohexane has been chosen from this number of solvents despite the fairly high viscosity of the polymer solution in it. It was found that solutions with low viscosity can be received, using toluene and hexane, however, the first one has a greater toxicity, and in case of the last one, the instability of emulsions during solvent removal process was observed.

Cationic surfactants such as dimethylalkylbenzylammonium chloride with the varying length of the alkyl radical have been used in the work. Based on the experimental data, it was concluded that there is an increase in the stability of emulsions at increase in length and dispersion of the alkyl radical of quaternary ammonium compound. The results of these studies have allowed to recommend the length of the alkyl radical of surfactant about C8-C18 and C10-C18 needed for preparation of IIR artificial latex with positively charged polymer particles.

It was interesting to study the possibility of applying the organosilicon surfactants, that are widely used in the synthesis of synthetic latex, for artificial latex preparation. Studies have shown that the use of organosilicon surfactants separately or in the mix with each other cannot produce stable emulsions of IIR solution, however when using a mixture of organosilicon surfactant with a cationic surfactant an opposite effect is observed. It was established that the optimum ratio of surfactants at which necessary stability of emulsions is reached is equal 1:2. It was also shown that the use of water insoluble organosilicon surfactant lowers the foaming during solvent stripping without buckling polymer suspensions.

The comparative analysis of mechanical-and-physical properties of the films received from butyl rubber solution and latex has been carried out. Based on the experimental data one can conclude that the butyl rubber latex films comparable in strength and operational parameters the films prepared from the solution.
POSSIBILITIES OF X-RAY MICROSCOPY FOR NONDESTRUCTIVE RESEARCH OF INTERNAL STRUCTURE OF POLYMER COMPOSITES

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Currently, research of internal structure of polymers and polymer composites are conducted mainly in vacuum using electron microscopes. Thus, only the surface of the chips and fractures is investigated, and sometimes the surface layers of materials are consistently being removed mechanically or by ion beam. But these destructive and costly methods do not give full and timely information about the internal structure.

Information about the internal structure of objects as well as 3D images can be obtained by X-ray radiation in air, in liquid phase and in a vacuum. Now, the resolution of 20-30 nm is attainable on synchrotrons, and with X-ray tubes - down to 50 nm. To enhance technical and economical characteristics of X-ray microscopes, a hybrid nanoscope (HN) was elaborated [1], which is a novel diagnostic device of economical class, in which a raster electronic and X-ray microscopes, as well as X-ray spectral analyzer, are optimally combined together (Fig. 1)

HN works as a scanning electron microscope with a resolution 1-5nm with object installation under electron beam. To go to the X-ray microscope mode with a resolution of 20-30nm, instead of an object under the beam an X-ray target is entered on a vacuum tight substrate of 0.1-10mkm thickness made of Be, Si, Si 3N 4, C, etc., followed by objects and X-ray detectors, placed on air.

With the aid of secondary electron detector, electron beam is focused accurately and timely on the target in scanning mode according to the image of target surface [2]. X-ray microscope can work in projection mode, when the electron beam is at the point and coordinate-sensitive detector is used. In scanning mode, X-ray radiation is recorded with the detector having variable input aperture. In the projection mode, 3D images are obtained with shots made at several fixed displacements of the beam, and in the scanning mode - using multiple detectors placed at different angles to the axis of the instrument. Visually, the possibilities of X-ray microscopy are shown with the images, made in X-ray and SEM mode for composites (Fig. 2, 3), consisting of the organic film with 270 mkm thickness and zinc particles, embedded in.

Fig. 1. Hybrid nanoscope.

Fig. 2. X-ray shot in HN. Fig. 3. SEM (FEI).

References:
RUBBER-POLYMERIC MODIFIERS "POLIPOR-RP", PRODUCED BY USING
THE TECHNIQUE OF HIGH-TEMPERATURE SHEAR-INDUCED GRINDING

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Annually in Russia about 900 000 tons of worn-out tires collect, but only the small part of
them are exposed to utilization therefore the problem of processing or a recycling of rubber
products, including worn-out tire covers is actual for the whole world. Now the special attention
is paid to problems of recycling waste of rubber industry which can become the most valuable
raw materials for modification of bitumen, as allow to replace primary polymeric materials
secondary raw materials. In recent years loads of roads have very strongly increased because of
sharp increase in streams of trucks and formation of "traffic jams" [1].

The required properties of the road can not be achieved using conventional bitumen.
During the construction of the road should be used modified bitumen. However, nearly all
polymer modified bitumen delaminate during storage, as well as a deterioration of their
properties. The idea of creating a composite asphalt binder that combines the advantages of
several types of modifiers is not new. But only at institute of chemical physics succeeded to
develop binary mixtures powder of a rubber crumb and SBS which is offered for introduction to
asphalt concrete mix by uniform falling asleep of the binary modifier in the mixer at the
bequeathing stage.

The aim this paper is the creation and to study properties of modifiers based on polymers
(SBS) and crumb rubber produced in rotor dispersers by using the technique of high-temperature
shear-induced grinding (HTSG) suitable for modification of asphalt "dry" method, as well as the
production of hybrid bitumen binders with micro- and nano-organized structure and high
resistance to cracking. Introduction of the binary mix received in rotor dispersators along with
bitumen at asphalt concrete production, passing a long and energy-intensive stage of preparation
of the modified bituminous knitting, it was possible thanks to very friable surface of powder
particles with a large amount of emptiness and canals into which at mixture it is capable to flow
bitumen and to break off a particle from within [2].

At the time of such hybrid modifier produced in the factory of "ENERGOTEX" (Russia,
Kursk oblast, Kurchatov) using new dispersants, which allows to obtain a fine powder with an
average particle size of about 80 microns [3].

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   on the properties of road asphalt binders containing thermoplastic and rubber crumb obtained by high-
   2016. № 3 (1012). P. 73-80.
CREATION OF POLYELECTROLYTE MICROCAPSULES
BASED ON PICKERING EMULSIONS AND NANOSIZED
TITANIUM DIOXIDE AND ALUMINIUM OXIDE PARTICLES

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Interesting perspectives associated with the use of micro and nanocapsules in the biotechnology, chemical synthesis, catalysis were opened recently. These objects were proposed to use as reactors with a limited volume, drug carriers, protective membranes for cells and enzymes in heterogeneous catalysis carrier materials for disperse dyes or removal of contaminants. A special problem takes place is encapsulation of hydrophobic compounds because such systems allow to stabilize the capsules phase separation of components, to protect the contents from exposure to the environment and to ensure the possibility of controlled release. A promising way to encapsulate functional compounds is sequential adsorption method which allows to create a stable adjustable shell thickness enables the use of a wide range of materials to create capsules.

The aim of this work is to create microreactors as which will act polyelectrolyte microcapsules on the basis of Pickering emulsion (PE) oil-in-water and nanosized titanium dioxide and aluminium oxide particles because of their unique photocatalytic and adsorption properties.

Commercial hydrophilic nanosized titanium dioxide (particle size ≤ 25 nm) with anatase structure and aluminium oxide (particle size ≤ 50 nm) with γ-structure hydrophobised with n-octadecylphosphonic acid were used as stabilizing PE particles; the hydrophobization process was carried out according to the improved method described in [1]. Acid coating surfaces of titanium dioxide is 22%. The same concentration of the acid has been used for aluminium oxide surface hydrophobization Stabilization of oil-in-water emulsion was carried out by self-organization of nanoparticles layer liquid phase interface. Then colloidosomes obtained was used as a template for the subsequent the layer-by-layer (L-b-L) deposition of oppositely charged polyelectrolytes. Poly(sodium 4-styrenesulfonate) (PSS) (negatively charged polyelectrolytes) and chitosane (low MM) or poly(fluorescent isothiocyanate allylamine hydrochloride) (FITC-labeled PAH) (positively charged polyelectrolyte) were used. The size of the obtained microcapsules is 3÷5 μm.

Stable colloidosomes have positive charged surface: ζ ~ 30 mV and ζ ~ 40 mV for nanosized titanium dioxide and aluminium oxide, respectively. After adding negatively charged PSS solution the surface was recharged, ζ ~ -40 mV. Next recharging with positive polyelectrolytes gives ζ ~ 60 mV. This shows that this systems are very stable.

It was shown that the stable polymeric microcapsules with the nanosized titanium dioxide and aluminium oxide can be prepared by L-b-L deposition of the polyelectrolytes on the PE. Polyelectrolyte shell can be formed using not only synthetic polyelectrolytes (PAH, PSS) but also biopolymers such as chitosane.

References:
Recently textile materials and products are developed that provide security and improve the quality of human life. Creation of a safe range of fabrics with antimicrobial properties is an urgent issue.

At the moment, different techniques, photonic technologies, laser processing, plasma discharge are used in order to give special properties to the different origin fibers. These methods offer great possibilities for modifying fibers and textile, but a significant disadvantage is the high outlay, as such processes require special expensive equipment and have specific limitations. Based on an analysis of literature data, the sol-gel technology that allows to create repeatable, controlled and ordered structure can be considered as a promising method of obtaining the necessary technically valuable properties.

The sol-gel synthesis involves the formation of a sol followed by passing it into a gel. A sol is a suspension of solid particles in the size range from 1 nm to 1 micron, which can be prepared by hydrolysis and partial condensation of alkoxides precursors and silicates. The conditions used for the preparation of sols solvent, pH, temperature, concentration, the sol concentration, determine the development of particles, as well as their resolution. The hydrolysis can be carried out both in acidic and alkaline medium. There are also non-aqueous sol-gel.

In this paper we consider the procedure of the synthesis of protective SiO$_2$ coating through the sol-gel method, study physical and mechanical properties and antimicrobial properties of the obtained materials.

According to the results of electron scanning microscopy the elemental composition of two film-forming solutions were investigated. The first solution contained zinc acetate SiK - 6.21%, ZnK - 3.98%. The second solution contained copper acetate SiK - 14.57%, CuK - 16.08%. The obtained data show that our technology provides consolidating of zinc acetate and copper nanoparticles on the surface of cellulose fabric fibers.

Cultures of S. aureus, E. coli, C. albicans, Ps. aeruginosa were used as the test microorganisms. The analysis of the results show that the dressed samples possess antimicrobial properties, efficiency after the zinc acetate treatment was: S. aureus - 80%, E. coli - 71.3%, C. albicans - 79.2%, Ps. aeruginosa - 25.9%. The efficacy after copper acetate treatment was: S. aureus - 90.7%, E. coli - 80.0%, C. albicans - 86.0%, Ps. aeruginosa - 27.8%. According to the obtained data, we can draw conclusion about the high antimicrobial properties of the treated samples. Moreover, the best indicators of antimicrobial activity have been revealed after the acetate treatment with.

During the study on determination of the breaking load, it was found that the impregnation compound does not affect the breaking indices of the study samples vary within, breaking load of the untreated sample is 209.1 N, breaking load of the treated sample is 212.6 N. The porosity indicators remain virtually unchanged compared to the untreated cloth 170.9 dm$^3$/m$^2$∙s, treated sample is 168.7 dm$^3$/m$^2$∙s. The porosity of the cotton fabric treated through the proposed composition comply with regulatory requirements for this group of fabrics.
Liquid crystal polymers (LCP) are promising materials for the production of organic electronics devices, micro electro mechanical systems, various sensors including biological ones [1]. Application of LCP with mesogenic side chains meets the requirements of devices miniaturization the most.

Currently, there are two ways to prepare polymers with mesogenic side groups [2, 3]. The first method is to obtain the vinyl monomers with mesogenic groups followed by copolymerization or homopolymerization with mesogenic or nonmesogenic compounds. The second method for the preparation is molecules addition of mesogenic groups to the polymer chain.

The objective of the research is the preparation of comb LCP from the polyacrylic acid and glycine.

In this work the second method was used for the preparation of LCP. The atactic polyacrylic acid was used as the primary polymer, and glycine (amino acetic acid) as the low molecular weight substance.

The reaction was carried out in a stirred tank reactor in solution. The mixture of ethylene glycol and distilled water was used as a solvent. The process was carried out at a temperature of 75-80 °C. The catalyst was n-toluene sulphonic acid in an amount of 1 % by weight of the amount of starting reagents.

During the process the starting reagents and the stock were analyzed for carboxyl groups content. IR spectroscopy was used for analysis of LCP.

Based on the results of the work some recommendations on the optimal conditions for the synthesis of liquid crystal polymer with meso groups in the side chains were proposed.

References:
Fillers are used to reduce the gas permeability have usually scaly or lamellated structure. Therefore, it is important to the ability to reduce the gas permeability of polyolefin products by creating a barrier layers of scaly fillers, in particular glass plates micron size, by creating products in a special multi-layer construction with the functional layers in the process of preparation of the compositions and the manufacture of products from them. The idea of reducing the gas permeability of polymeric material with glass filler plate is to reduce the area available for the diffusion of substances or increasing the diffusion path length. Moreover, the orientation and shape of the particles play a greater role than the distance between the particles. The rheological and mechanical properties of filled polymers are important in choosing the optimum processing conditions to achieve the planar orientation of the particles.

In this work carried out a comprehensive analysis of the influence of plate glass fillers GF300M epoxy and GF003 amino at 5, 10 and 15 wt.% on the mechanical-and-physical and rheological properties of high density polyethylene blends.

The filled polymer composites were obtained on a twin-screw extruder Werner & Pfleiderer ZSK 25, with the ratio L/D 40. Feeding filler conducted in the melt zone of the extruder feeder Licos.p.a. Italy. Standard samples for physical and mechanical tests were made on an injection molding machine ARBURG 320 M / 850-210.

Determination of rheological characteristics of the samples was carried out by rotational viscometry at AR2000. TA Instruments (US) with the measuring system in the shear rate range of plane-plane 1-600 1/s at temperatures of 180-220°C. Physical and mechanical characteristics of the compositions of samples in tension and bending were evaluated in accordance with GOST 11262 and GOST 4648 on a tensile testing machine Zwick Roell Z050 at 23°C.

Evaluation of the compositions melt flow (MFI) at a load of 5 kg and a temperature of 190 °C showed that the introduction of the plate glass filler increases the mass flow rate of from 0.40 to 0.79 g / 10 min and 0.82 g / 10 min and for GF003 amino GF300M epoxy, respectively, in connection with a platelet filler particle orientation in the direction of flow and slip relative to each other.

Analysis melt flow curves showed that the compositions are pseudoplastic fluids: the viscosity decreases with increasing shear rate. Increasing filler concentration and an increase in average particle diameter, its characteristic proportional relation, increases the melt viscosity and the processing temperature. For samples containing 15 wt.% of glass filler plate, at low values of shear velocities higher shear stress and shear rate when the order of 200 1/s shear value of voltage drop as compared with other samples. Flow curves obtained at different temperatures, and the like are aligned along the axis of the shear shear parallel to themselves.

Introduction of the plate glass filler increases the modulus of elasticity in tension and bending at 1.5-2. This filler GF300M epoxy has a more pronounced reinforcing effect than the GF003 amino, which is a consequence of the high aspect ratio of the first. It should be noted that when the filler content 15 wt. % GF300M epoxy - at 3-5 times - sharply reduced strength and tensile elongation due to the presence of filler particles and unoriented areas overlap each other adjacent scales, which disrupts the continuity of the polymer phases.

Thus, to obtain products with optimum performance properties of the composition with the glass flake filler must be processed at lower shear stresses and high temperatures to minimize degradation of the filler.
Surfactants, especially polymeric or oligomeric, are widely used in various industries having low adsorption selectivity. They are used to stabilize the dispersion, rheology control of colloid systems, improve wetting [1].

We have investigated the modification yellow iron oxide pigment by polycarboxylate surfactants based polyethylene glycol.

Yellow iron oxide pigment was prepared by the oxidation of Fe$^{2+}$ and hydrolysis of Fe$^{3+}$ in ferrous sulfate solution medium using goethite nuclei. Synthesis was performed at 60 degrees. Surfactant treatment was carried out after washing the pigment.

The water-soluble surfactant based on polyethylene glycol oligomers, glycidyl ether and methacrylic acid have been synthesized in isopropl alcohol medium in the presence of azobisisobutyronitrile initiator [2].

It shows the effect of the modification on the technological properties of yellow iron oxide pigment.

It is established that the carboxyl-containing polymer surfactant chemisorbed on the surface of a goethite particle, significantly change its properties, especially twice reducing its oil absorption, which can significantly increase the content of the polymer composite material and more than ten times the accelerate the dispersion process is extremely energy-intensive step of producing pigmented materials. Lightness and hue of pigments have not changed.

References:


MODIFICATION POLYSILOXANES AND WATER REPELLENTS
BASED ON THEM

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The study based on the water-repellent composite organoalkoxysiloxanes and active filler to further assess the possibility of their use in water protection compositions for building materials.

To create a hydrophobic surface textured currently uses various methods, including the use of organic and inorganic fillers with a multimodal particle size distribution, embedded in a matrix of a hydrophobic material.

As hydrophobic matrix material used organoalkoxysiloxanes prepared by partial hydrolysis and condensation of methyltrimethoxysilane and octyltriethoxysilane.

The resulting organoalkoxysiloxanes introduced inorganic fillers, which was chosen as the aerosil, both with treated and with untreated surface (grade R-812, R-8200, HDK H-2000, A-380) was selected. The aerosil content in organoalkoxysiloxanes fluid was 2-10%. Introduction aerosil was performed by dispersing at gomogonizatore. The thus prepared composite repellents were opalescent viscous liquid, which further examined for stability over time. It was found that only one composition containing aerosil R-812 is stable for a long time (12 months). Other compositions for 1-3 weeks ceased to be uniform, observed the formation of lower second phase in the form of a very thick gel. This is probably due to the large particle size have aerosil R-8200 and HDK H-2000, compared with R-812, and have a hydrophilic surface aerosil A-380. Therefore, compositions containing organoalkoxysiloxanes and aerosil R-812 were chosen for further studies on the preparation of hydrophobic coatings.

A composite water repellents based on organoalkoxysiloxanes and active filler. We found that the most stable compositions are obtained by using as a modified filler aerosil R-812. Deposited on the surface of aerosil gives it a strong hydrophobic effect. Aerosil combined with octylalkoxysiloxanes performed better on such indicators as the water absorption.
Hydrolytic polycondensation (HPC) of organosilicon monomers - one of the most important methods of modern technology of polyorganosiloxanes in the industry. At present time much attention is paid to improving the HPC methods and search for alternative ways of its realization. Among the research in this regard, a special place is occupied processes of HPC organosilicon monomers in homogeneous, non-aqueous media, in which water is generated during the process.

We have shown that rapid HPC monomers is in non-aqueous system diorganodichlorosilanes RR’SiCl2 - carbamide-1,3-diketone-organic solvent. The source of the water molecules to hydrolyze the chlorosilanes in this system is a dehydration condensation of the ketone with carbamide, which comes only with the addition of chlorosilane. Due to the presence of two interrelated coupled reactions (hydrolysis and dehydrocondensation), the HPC is developing as a typical cascade process.

It is characteristic that in this system the water generated at the molecular level and in a strictly stoichiometric amounts [1]. This allows to fine regulation of the speed of its entry into the reaction zone and the conditions of formation of polyorganosiloxanes.

Investigations have established that cascading HPC chlorosilanes retained by replacing 1,3-diketones to simple ketones – f.e., acetone, cyclohexanone, acetophenone, etc. are developing similar way [2]. In all cases, polyorganosiloxanes of cyclic and of a linear structure formed with high yields, and also a nitrogenous base hydrochloride are formed. The ratio of reactants (chlorosilane-carbamide-ketone) and the nature of the solvent on the yield, composition and structure of the resulting oligomers had been investigated. In the case of the HPC in polar solvents, the proportion of linear oligosiloxanes reaches ≤70%. Changing the nature of the ketone and the ratio of chlorosilane-carbamide can be controlled by the structure of cyclosiloxanes (as in the case of acetylacetone the output of hexamethylocyclotrisiloxane reaches 65%).

The structure and composition of formed products were studied by NMR 1H, 29Si, GLC, GPC.

Acknowledgements
This work was supported by RFBR (project № 15-03-05235).

References:
NEW NON-PHTHALATE PLASTICIZERS USING ESTERS OF POLYATOMIC ALCOHOLS

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Most plasticizers are plasticizer esters. Currently, more than 50 types of plasticizer esters are being produced, most of which are used for modification of polyvinyl chloride (PVC). The most common PVC plasticizers are phthalate ones: dioctyl phthalate, dibutyl phthalate. Their significant drawback is high toxicity, also some plasticizer have volatilization and poor compatibility with polymers.

Therefore, the development of new competitive technological and eco non-phthalate plasticizers is a promising direction.

Esters of polyatomic alcohols as a promising plasticizers have the practical value to date. A universal polyalcohol among them is trimethylolpropane (TMP) which is a non-toxic and safe product that can be used for producing esters. Heavy complicated trimethylolpropane esters are used as lubricants for the aviation industry, and the light ones can be used as plasticizers for PVC compositions.

The objective of the research is the preparation of a non-phthalate plasticizer based on trimethylolpropane esters.

Synthesis of TMP esters was performed by azeotropic esterification. The reaction was conducted in the presence of azeotropic agents (benzene or toluene). Concentrated orthophosphoric acid (87 wt %) of about 1% by weight of the reaction mixture was used as a catalyst. For preparation of trimethylolpropane esters the process was carried out with an excess of the appropriate acid, there is a 6:1 mole ratio between acid and trimethylolpropane. The reaction time is 10-15 hours. The yield of esters is not less than 98% by weight.

Physical and chemical characteristics (flash point, acid number, pour point, the hazard class) of plasticizers were defined for TMP esters. Comparative characteristics of TMP esters and phthalate plasticizers are shown.

The results obtained suggest that trimethylolpropane esters may serve as good plasticizers for PVC compounds and other polymeric materials.

Acknowledgements
The work was supported by the Russian Federal Property Fund within the framework of a research project № 16-08-00383a.
CREATION OF DEVICE BASED ON CONTINUOUS REACTOR TO PRODUCE A MODIFIED ASPHALT BINDER

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The use of impregnating compositions based on modified bitumen, is one of the ways to solve the problem of protection of asphalt concrete pavement on the negative impact of natural and man-made disasters to increase their lifetime [1].

Earlier we reported that for the modification of asphalt binder (Petroleum road bitumen BND 60/90), we chose petroleum resin (PR) "Sibplast", which is a product of the thermal polymerization of C9 fraction. Modification of BND 60/90 was carried out in a steel reactor with an overhead stirrer by introducing into the bitumen PR (from 5 to 15 wt.%) heated to a temperature of 160 °C, and then maintaining it at a temperature not exceeding 180 °C, for 90 min. The scheme for preparing the modified binder in this case was periodic [2].

Improved technology for producing bitumen, has a device for producing bitumen based on a continuous reactor. Installation consists of two heated steel tanks in which are respectively bitumen and PR. According to the heated bitumen and pipeline pumps PR receives a continuous steel reactor, where they are mixing. Operations for heating and applying components and mixing them, are a computer. In this way it is possible to accurately calculate the flow of components to monitor the temperature and residence time in the reactor.

In continuous modification is easier to control the final properties of the finished product compared to obtain a periodic pattern.

Received in this modified installation binder resin is a homogeneous dark brown to black color with depth of needle penetration at 25 °C, 0.1 mm - from 40 to 60, softening point «Ring and Ball», °C - from 40 to 60 and the ductility at 25 °C - 70 sm.

The modified binder was combined with a further solvent such as "Nefras" for protective impregnating composition of asphalt concrete pavement. These tests of asphalt concrete pavement coated with an impregnating layer in comparison with control samples (without application) confirm the reduction of water saturation of the main operational properties of asphalt concrete. At the moment, work is underway to modify PR of various grades of bitumen for use as the main component of the composition of the protective impregnating compositions.

Acknowledgements

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References:


Polymer electrolyte membrane fuel cells (PEMFC), which transform fuel chemical energy directly into electricity, have attracted much attention during the last decade, due to the growing interest in the generation of renewable energy for application in stationary and portable devices [1-3]. PEMFC are promising systems to deliver renewable energy because of their low environmental impact when supplied with hydrogen-containing fuels, such as methanol, ethanol, added to the capacity of producing high energy densities [1-5]. The development of management composition methods, structure, nanoparticles (NP) properties, revealing of the nanostructured composites controlled formation and stabilization conditions, peculiarities of mechanisms current forming reactions in the NP presence, the influence of nanomaterials morphology, structure, phase composition on the reactivity, are a fundamental objective of physical chemistry and fine chemical technologies for the decision of modern power engineering problems [1-3].

Modified polymer membranes Nafion with a thickness of less than 0.2 mm were applied as nano-structured matrix-substrates. Polymer membranes are widely used in the energy sources due to their high unipolar proton conductivity [1-5]. Modification of electrode-metallic composites was performed by metal nanoparticles, received with chemical reduction of metal ions in water-organic reverse micelle solutions [3]. The application of reverse micelles as nanoreactors in the synthesis allows to obtain stable metal NP with controlled size and shape [4].

The thin-film metal-polymer bimetal platinum nanocomposites can be used as the basis of high performance miniature flexible generators of energy [4]. Optimization of the metal nanoparticles formation conditions in polymer matrix allows improving the functional characteristics of the energy sources membrane-electrode blocks. In addition, the metal-polymer nanocomposites promote additional catalytic oxidation of fuel, preventing its penetration through the polymer membrane (crossover).

Initial solutions of bimetallic Pt-Ru and Pt-Pd nanoparticles were prepared in water organic solutions by mixing two microemulsions [1,5] with platinum metal salts and NaBH\textsubscript{4} as a reducing agent. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) served as a surfactant. Varying the synthesis conditions one can control the nanoparticles size, content and functional properties. By means of the electron microscopy, X-ray phase analysis and small angle scattering it was performed the investigation of nanoparticle and nanocomposite functional properties. The obtained bimetal/polymer electrodes containing nanoparticles of different composition, size and shape, can be used as functional membrane-electrode materials for high-performance electrochemical fuel conversion of chemical energy sources.

**Acknowledgements**

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**References:**

THE DEVELOPMENT OF CATALYTICAL ACTIVE POLYMER NANOCOMPOSITES WITH BIMETALLIC PLATINUM METAL NANOPARTICLES

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The development of highly active and stable nanoelectrocatalysts for portable chemical sources – fuel cells (FC) is one of the fundamental problems of modern physical chemistry, science and technology [1-3]. The composition, size, shape, and distribution of metal nanoparticles incorporated to a polymer membrane play a key role in efforts to improve the efficiency, stability, and selectivity of energy conversion in the proton exchange membrane (PEM) fuel cells. There are experimental data on the synthesis of platinum metal nanoparticles incorporated into the commercial Nafion®-type membranes [1-5]. Modification of polymeric Nafion films with platinum metal nanoparticles improves the catalyst stability in FC and serves to avoid the crossover effect, i.e., diffusion of fuel molecules through a membrane towards oxidizing agent. However, the above mentioned works contain no data on the relationship of synthesis conditions, sizes, and distribution of metal nanoparticles in a membrane with their catalytic activities, as well as with the electrochemical parameters of hydrogen containing fuel conversion. The aim of the present study was to establish the influence of the metal/polymers Pt-Pd/Nf synthesis parameters on the catalytic activity of nanocomposites in the hydrogen oxidation and oxygen reduction reactions.

Initial solutions of bimetallic Pt-Pd nanoparticles were prepared in water organic solutions by mixing two microemulsions with platinum metal salts and NaBH₄ as a reducing agent [1, 2]. As surfactant, a 0.2 M solution of Triton X-100 was used (Acros Organics, United States). Varying the synthesis conditions one can control the nanoparticles size, content and functional properties. By means of the modern physico-chemical research methods, as electron microscopy, x-ray photoelectron spectroscopy, cyclic voltammetry (CVA) it was performed the investigation of nanoparticle and nanocomposite functional properties.

According to electron microscopy data nanoparticles with sizes from 2 to 8 nm and smaller nanoparticles make the main contribution to the formation of nanocomposites. From CVA analysis it was concluded that the catalytic activity of Pt-Pd/Nf nanocomposites containing the excess of platinum (3:1) is higher than that of Pt-Pd/Nf nanocomposites with a lower platinum content (1:1 and 1:3). The highest content of platinum metals in the nanocomposites corresponding to the highest catalytic conversion of hydrogen is 0.41±0.05 mg cm⁻². It was found that when reducing the size of metal nanoparticles (less than 5 nm) catalytic activity of metal/polymer nanocomposites (current density, catalytically active surface area) increases [1,2].

Acknowledgements

The work was supported by RFBR (grant № 13-08-12407-ofi_m2).

References:
Currently anodic electrodeposition is one of the common ways of coloring water-thinnable paints. Water-oligomeric film-formers for anodic electrodeposition are polyelectrolytes. Their aqueous solutions are in the range of working concentrations and pH values are colloidal in nature. As an object of research lacquer KCh-0125 has been selected, the main component of which is maleated polybutadiene.

It is known that coatings produced by electrodeposition, cured at high temperatures (180 °C and above).

In order to reduce the energy intensity of production of polymer coatings, to improve their physical and mechanical properties and extend the color gamut of paints for electrodeposition as modifiers were selected metalloporphyrins: copper complex of methylpheophorbid (a) and cobalt complex of pheofitin (II).

Viscometric research dilute solutions of unmodified and modified varnish compositions based on KCh-0125 showed that the introduction of the modifier does not alter the concentration dependence of the anomalous form the reduced viscosity $\eta_{\text{spec}} / C = f(C)$, which is characteristic of aqueous solutions of polyelectrolytes.

The value of the $\zeta$-potential is one of the important indicators of stability of colloidal systems and their electrophoretic mobility. Upon dilution of the polymer solution it is rearranged micelles, whereby the diffuse layer expands. It facilitates the transition from the adsorption layer in diffuse growing number of counter-ions, their concentration in the dispersion medium increases, which causes an increase in the pH value and the $\zeta$-potential and shows a high aggregate stability of the systems studied. The resulting dependence of the $\zeta$-potential of the solution concentration is typical of colloidal systems.

Comparative evaluation of the degree of curing coating was carried out on a gel. The decrease of the modified coatings cure temperature to 160 °C does not reduce the content of gel fraction.

Introduction copper complex of methylpheophorbid (a) attached to the polymer coating of emerald green.

Modified electrodeposited coatings are highly protective and physical and mechanical properties.

Acknowledgements
This work was supported by the Russian Science Foundation (project No. 14-23-00204).
GLOBULAR PROTEIN ADSORPTION EQUILIBRIUM AND THERMODYNAMICS ON ULTRAFILTRATION MEMBRANES

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The significant interest to the investigations of protein adsorption on membranes’ surface is due to the degree of influence on their mass-exchange properties during ultrafiltration process. The importance of choice of optimal “equilibrium model” for systems under consideration is caused on the one hand by the necessity of reliable prediction of equilibrium state protein/membrane and educing the main factors of “influence” and on the other hand – it is the essential part of kinetic model development and the calculation of sorption/desorption kinetic parameters.

In present work membranes (Molecular Weight Cut Off (MWCO) 25–50 kDa) based on co-polyamides with sulfonate groups (PA-10(-)) and also poly-\(m\)-phenyleneisophtalamide (PA) and its mixtures with co-polymer of acrylonitrile with DMDAAC (PA-10(+) were the subjects of research.

For the determination of membrane/protein interaction mechanism and educing membrane adsorption activity regulation factors the solutions of lisozyme (Lys) (pI=11,0 \(M_w=14,3\) kDa) and myoglobin (Myo) (pI=7,0 \(M_w=16,8\) kDa) were used.

For adsorption equilibrium specification Langmuir, Freundlich and Temkin two-parameter models were chosen [1, 2]. The results mathematical treatment of experimental data are presented in a Table

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Conditions</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>Temkin isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>Lys, pH=6,86</td>
<td>(Q_m), b, (R^2)</td>
<td>(P), (1/n), (R^2)</td>
<td>(A_T), (b_T), (R^2)</td>
</tr>
<tr>
<td></td>
<td>Lys, pH=7,0</td>
<td>0,150, 0,00178, 0,9927</td>
<td>0,00184, 0,57, 0,8766</td>
<td>0,0171, 73301, 0,9921</td>
</tr>
<tr>
<td></td>
<td>Myo, pH=8,0</td>
<td>0,103, 0,00147, 0,9967</td>
<td>0,00128, 0,55, 0,9778</td>
<td>0,0151, 112107, 0,9892</td>
</tr>
<tr>
<td>PA-10(-)</td>
<td>Lys, pH=6,86</td>
<td>0,378, 0,00199, 0,9761</td>
<td>0,00474, 0,57, 0,8401</td>
<td>0,0189, 28742, 0,9728</td>
</tr>
<tr>
<td></td>
<td>Myo, pH=7,0</td>
<td>0,119, 0,00153, 0,9967</td>
<td>0,00141, 0,56, 0,9529</td>
<td>0,0158, 96404, 0,9982</td>
</tr>
<tr>
<td></td>
<td>Myo, pH=8,0</td>
<td>0,0556, 0,000918, 0,9827</td>
<td>0,000279, 0,65, 0,9750</td>
<td>0,0118, 225234, 0,9639</td>
</tr>
<tr>
<td>PA-10(+)</td>
<td>Lys, pH=6,86</td>
<td>0,0168, 0,00299, 0,8582</td>
<td>0,00242, 0,24, 0,6609</td>
<td>0,0283, 635274, 0,8379</td>
</tr>
<tr>
<td></td>
<td>Myo, pH=7,0</td>
<td>0,0859, 0,00156, 0,9788</td>
<td>0,00147, 0,51, 0,9881</td>
<td>0,017, 137643, 0,9790</td>
</tr>
<tr>
<td></td>
<td>Myo, pH=8,0</td>
<td>0,215, 0,000886, 0,9958</td>
<td>0,000782, 0,70, 0,9181</td>
<td>0,0112, 58023, 0,9936</td>
</tr>
</tbody>
</table>

References:
1. K.Y. Foo, B.H. Hamied Insights into the modeling of adsorption isotherms // Chemical engineering journal. 2010, 156, P. 2-10
The problem of environmental by a wastage of polymeric materials is one of a set of problems which harmful influence a state of environment. At the same time to contain in a wastage valuable components which can be used as secondary raw materials. To the main ways of a salvage of plasts burial, combustion, secondary processing, thermal decomposition by a pyrolysis, decomposition treat with receiving low-molecular products.

One of efficient ways of processing of a polymeric wastage is a pyrolysis. Process represents thermal decomposition of plastic under the influence of high temperatures in lack of oxygen. By means of a pyrolysis receive: oven fuel, syntheses gasis, thermal energy and liquid fuels (analog of solar oil). Also, it is possible to achieve decrease in volumes of burial of garbage in the country and to gain notable economic effect as a result of use gaseous and fluid pyrolized species with high combustion heat.

Depending on temperature of process distinguish three types of a pyrolysis: the low-temperature, medium temperature and high-temperature.

The low-temperature pyrolysis takes place at a temperature of 450 – 900 °C, the gas discharge at such pyrolysis is extremely small, and amount of pitches, oils, a fixed residue is maximum. A medium temperature pyrolysis proceeds in the range from 550 – 800 °C, gives vent larger amount of gas with smaller combustion heat, quantity of the fluid rest and coke. High-temperature pyrolysis takes place at a temperature over 900 °C, the gas discharge at this way is maximum, and the quantity of a wastage is minimized. [1]

Advantages of the low-temperature pyrolysis: receiving pyrolysis oils which can be used in production of plastic; selection of pyrolysis gas which goes for ensuring production of power supplies; minimum quantity of harmful substances; low sensitivity to a feed stock. Advantages of a high-temperature pyrolysis: sorting of a wastage is not required; the minimum mass of an ash content which can be used in the structural and production purposes; the complete decomposition of all dangerous substances. The pyrolysis oils received in such a way have sufficient degree of purity and do not demand cleaning.

Light-end products can be used for technological needs of installation and for heating of production rooms. Fluid products are used for receiving heat carriers and represent mix of various hydrocarbons. The range of use of solid pyrolized species is rather wide: different components of protective structures, greasings, emulsions, treating materials, etc. [2].

References:
Interest in full of building materials in which the sulfur-based composition used as a binder, due to technical advantages - rapid solidification and curing, resistance to aggressive media, water repellency. Sulfur modification by introducing polymer additives gives it a set of additional properties such as increased strength, resistance to oxidation, adhesion, and overlaying characteristics and others. In addition, the use of sulfur compositions and polymeric sulfur compounds with the modifier will allow the use of additional amounts of sulfur in the production of filled construction materials.

For binders as reactive modifiers were selected cyclic diene hydrocarbons are: dicyclopentadiene (DCPD), and 5-ethylidene-2-norbornene (ENB), capable of entering in the copolymerization with the sulfur to form organic polysulfides. It has been studied the influence of the conditions of interaction of sulfur and modifiers in an amount of 0-5 wt. % for the formation of organic polysulfides, because this range of concentrations has not been previously studied and practically is not described in the literature. It has been found that by using a modifier in an amount of 3.2 wt. %, With 15-30 minutes duration of the process, the organic polysulfide in the composition is 15-25 wt.%.

With increasing temperature, the content of organic polysulfides in the reaction mixture increases, suggesting radical process. At 160-180°C the viscosity increase and yield polymer compounds is 25 wt.%. The such temperature apparently increases the rate of biradical formation •S₈•, which leads to an increase in the content of polymeric compounds in the composition.

The modifier administration order for influence to the yields of polymeric compounds was also investigated. Liquid sulfur modifier is introduced into the melt with stirring or discretely premixing solid granulated sulfur modifier further joint with melting and stirring at a temperature of 140°C. It has been found that the premixing of solid sulfur modifier can increase the yield of polymeric compounds by 30-40% compared to the direct feed modifier in the melt under the same conditions.
STUDY OF SWELLING SYNTHESIZED POLYSULFIDE RUBBER

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Sealants on the basis of polysulphidic oligomer (PSO), first of all, on the basis of liquid thiokols, have found broad application in the aviation industry, mechanical engineering and in construction, thanks to a unique complex of properties – an outstanding oil and petrol resistance and a possibility of long-term operation in a wide temperature interval.

Operational materials on a basis the thiokol of rubbers are possible only in water solutions of acids and alkalis small and average (for alkalis) concentration [1, 2].

In this regard, the purpose of the present section of work was studying of influence of solvent on swelling speed, and also to study on spatial structure and properties of the received cured stock on the basis of a dichlorohydrin (DHGO), epichlorohydrin (EHGO) and mix DHGO and EHGO in the ratio 1:1. Polysulphidic cured stock aren't dissolved in alcohols, aromatic and aliphatic hydrocarbons. When comparing swelling capacity of cured stock received on the basis of EHGO well are dissolved in the given solvents, cured stock on the basis of DHGO are almost not dissolved, but bulk up in below the given solvents, and mix of cured stock in the ratio 1:1 is rather well dissolved than DHGO, but its solubility is less than at EHGO.

Swelling (1 mol, 30°C) vulcanizates polysulfide rubbers in various media
(in % by volume)

<table>
<thead>
<tr>
<th>№</th>
<th>Medium</th>
<th>DHGO</th>
<th>EHGO</th>
<th>DHGO: EHGO (1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
<td>2</td>
<td>1,3</td>
<td>1,7</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>3</td>
<td>2,4</td>
<td>2,4</td>
</tr>
<tr>
<td>3</td>
<td>Ethyl alcohol</td>
<td>0</td>
<td>0,14</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Acetone</td>
<td>0</td>
<td>0,18</td>
<td>0,15</td>
</tr>
<tr>
<td>5</td>
<td>Petrol</td>
<td>0,27</td>
<td>0,22</td>
<td>0,22</td>
</tr>
<tr>
<td>6</td>
<td>NaOH 20%</td>
<td>1,5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>NaOH 50%</td>
<td></td>
<td></td>
<td>destroyed</td>
</tr>
<tr>
<td>8</td>
<td>H₂SO₄ 10%</td>
<td>2,1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>H₂SO₄ 50%</td>
<td></td>
<td></td>
<td>destroyed</td>
</tr>
<tr>
<td>10</td>
<td>Dibutilftalat</td>
<td>2,4</td>
<td>1,5</td>
<td>1,8</td>
</tr>
<tr>
<td>11</td>
<td>Water</td>
<td>2</td>
<td>1,5</td>
<td>2</td>
</tr>
</tbody>
</table>

Thus, it is possible to assume that cured stock on the basis of DHGO more spatially sewed, than EHGO and mix EHGO and DHGO. From the obtained data it is possible to tell that the received cured stock are resistant to aggressive actions and organic solvents, and high gasoline resistance of polysulphidic cured stock causes it broad application, despite rather low frost resistance.

References:


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THE STUDY OF THE CHEMICAL AND ELECTROCHEMICAL ETCHING OF METAL FROM THE SURFACE OF THE CARBON POLYCRYSTAL

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The presence on the surface of polycrystalline carbon PCD metal catalysts reduces their properties due to a difference in coefficient of thermal expansion between the diamond grains and a catalyst that can lead to cracking during use. High temperature of PCD polycrystalline sample (Fig. 1) at its operation in the cutting area leads to reverse phase transition diamond - graphite. This phenomenon decreases the mechanical properties of the tool. In order to improve the wear resistance characteristics of polycrystalline diamond produced using metal catalysts, metal etching process is investigated with the working surface area of the polycrystalline.

Two experiments of etching types were conducted: chemical and electrochemical. Chemical etching was conducted with aqua regia and a mixture of hydrofluoric and nitric acids, electrochemical etching - sulfuric acid with predetermined current mode and concentration. The qualitative and quantitative analysis of elements on the depth of the samples from the surface of a polycrystalline diamond after etching (Fig. 1) were obtained by scanning electron microscopy. In work conclusions about the most optimal etching conditions.

Fig. 1. Polycrystalline cutter (1 – polycrystalline PCD, 2 – hard alloy).
Novel granular organic-inorganic surface molecularly imprinted polymers (MIPs) based on 2-hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were prepared by co-polymerization on the surface of selenium (Se) nanoparticles stabilized with poly(vinyl pyrrolidone) (PVP) at different concentrations of cholesterol as a template molecule. The obtained compounds are intended for use as selective hemosorbents in efferent therapy of hypercholesterolemia. The sorbents were characterized by scanning electron microscopy (SEM), infrared spectroscopy (IR) and sorption experiments. It was revealed that MIPs possess more pronounced porous structure as compared to that of the reference non-imprinted polymer (NIP). The influence of the amount of introduced cholesterol template on physico-chemical and sorption properties of MIPs was investigated.

IR spectroscopy and thermodynamic studies showed that the affinity of MIPs towards cholesterol is related to multi-point polyfunctional binding of adsorbate in complementary cavities or imprint sites; hydrogen bonds play the key role in recognition of the target molecule. The formation of the surface sorption layer in the MIPs facilitates availability of imprint sites and enhances the efficiency of specific cholesterol binding. The Langmuir, Freundlich, Temkin and BET model isotherms were used for interpreting the experimental data on the equilibrium sorption of cholesterol. Homogeneous distribution of cholesterol in the sorption monolayer, as well as the contribution of the specific binding to the sorption by MIPs, was observed with increasing amount of the template introduced (Fig. 1). In this case, the presence of easily accessible thermodynamically uniform imprint sites in the surface imprinted layer led to the growth of specific binding capacity of sorbents.

Fig. 1. Experimental (1) and model (2–5) sorption isotherms of cholesterol onto NIP (a), MIP-4 (b) and MIP-6 (c).

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SYNTHESIS AND MODIFICATION OF HYBRID ORGANIC-INORGANIC MOLECULARLY IMPRINTED POLYMERS BY BORATE GROUPS FOR HIGH SPECIFIC UPTAKE OF GLUCOSE

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The molecular recognition of carbohydrates, especially glucose, becomes remarkable due to their importance as biomarkers in different biological systems. In addition, selective uptake of glucose is actual for developing new approaches to the treatment of hyperglycemia and correction of blood glucose levels. Molecularly imprinted polymers (MIPs) for these purposes seem a viable alternative to expensive affine sorbents.

Novel granular organic-inorganic molecularly imprinted polymers (MIPs) based on 2-hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were prepared by co-polymerization on the surface of selenium (Se) stabilized with poly(vinyl pyrrolidone) (PVP) nanoparticles (Se/PVP). Reactions of reduction of red amorphous Se (α-form) in the acidic environment of ascorbic acid and in alkaline medium β-mercaptoethanol were previously studied; the reactions were carried out in an aqueous solution of PVP (MW = 55 th.) directly. The dynamic light scattering study showed the formation of stable globular nanoparticles; the average values of the hydrodynamic radius (Rh) of Se/PVP nanoparticles were about 49 and 34 nm in acidic and alkaline medium, respectively. HEMA-EGDMA@Se/PVP hybrid beads were synthesized under varying physico-chemical synthesis conditions (acidic or alkaline environment). The ratio of HEMA to EGDMA was studied as well. The acidic environment was found to be better for the preparation of hybrid polymer beads in a narrow range of particle size. The surface HEMA-EGDMA layer was molecularly imprinted with glucose templates (6 mol%). The modification of HEMA-EGDMA@Se/PVP matrix with orthoboric acid (6 mol%) that forms reversible covalent bonds with 1,2-cis- or cis-1,3-diols was studied, too. Therefore, we tried to create additional specific sorption centers in sorbents, as well as to prevent distribution of the associated glucose dimer and trimer molecules in the HEMA-EGDMA layer during molecular imprinting process. Thus, we tried to ensure the formation of highly specific imprint site around a single template molecule.

The following samples of sorbents were prepared: the non-modified non-imprinted polymer (NIP) as the reference sorbent, the modified with boric affine groups non-imprinted polymer (Aff-NIP), the polymer molecularly imprinted with glucose (MIP), and the imprinted polymer that was additionally modified with boric affine groups (Aff-MIP). The presence of boric affine groups in the matrix resulted in the formation of sorption sites with high specific affinity to glucose. In addition, thermodynamics of sorption showed different nature of specific affinity of imprint sites to glucose in the MIP and the Aff-MIP networks.

Acknowledgements

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THE USE OF RUTHENIUM-CONTAINING POLYMERIC CATALYSTS IN HYDROGENATION REACTION OF LEVULINIC ACID

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Gamma-valerolactone (GVL), which is accessible from renewable lignocellulosic biomass, has been suggested as a potential additive to gasoline, and the precursor for synthesis of polymers and fine chemicals. GVL can be produced by the selective hydrogenation of levulinic acid (LA) using various heterogeneous catalysts based on noble metals, such as Ru, Pd and Pt [1]. Ru/C is the most promising commercial catalyst for hydrogenation of LA [2]. New heterogeneous catalytic systems based on polymer-stabilized Ru-containing nanoparticles (NPs) can serve as an alternative to commercial Ru/C.

The key factor influencing the behavior of Ru-containing catalysts of LA hydrogenation is the size and dispersity of Ru-containing NPs [2]. The use of nanoscale metal particles in catalysis is one of the most fast-growing field of catalysis due to the fact that the decrease in particle size results in drastic increase of the number of catalytic sites involved in the process, and, consequently, in the increase of catalytic activity at low metal content. However, one of the main issues arising during the use of metal NPs is their low stability. Polymers with different functional groups (in particular, hypercrosslinked polystyrene (HPS)) can be used as NP stabilizers and supports. The use of polymers allows achieving high dispersion of metal particles along with ensuring the stability of their catalytic properties (prevention of aggregation and leaching). At present, HPS-based catalysts are successfully used in a wide range of hydrogenation reactions and exhibit high activity and selectivity [3]. Thus, we propose to use HPS-stabilized Ru-containing NPs as a catalyst of selective hydrogenation of LA to GVL.

In this work, the series of HPS-based Ru-containing catalysts was synthesized at variation of the type of polymer (bearing amine-groups or non-functionalized) and Ru loading. Catalytic properties of synthesized Ru/HPS systems were compared to commercial 5%-Ru/C in the reaction of LA hydrogenation to GVL. The hydrogenation reaction was carried out in Parr Series 5000 Multiple Reactor System (autoclave type reactor) at a stirring rate of 1500 rpm, at variation of process temperature (80-150°C), hydrogen pressure (1-4 MPa) and LA-to-catalyst ratio (50-200 g/g). Water was used as a solvent (volume of liquid phase was 50 mL). Samples of reaction mixture were analyzed via HPLC.

Comparison of synthesized HPS-based Ru-containing systems with commercial 5%-Ru/C showed that the Ru/HPS catalysts revealed higher activity and nearly 100% selectivity, i.e. the catalyst 5%-Ru/HPS prepared while using the HPS bearing amino-groups as a support was shown to allow carrying out the hydrogenation of LA in aqueous medium at mild reaction conditions (100°C and 2 MPa of hydrogen partial pressure) with high yields of GVL (not less than 99% for less than 2 h of reaction duration). It is noteworthy that at present there are no data on the testing of polymer-stabilized Ru NPs in the process of hydrogenation LA to GVL and proposed approaches are promising and completely new.

Acknowledgements

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References:
Polymeric cryogels are macroporous gel matrices formed in non-deeply frozen solutions or colloidal dispersions of suitable monomeric or polymeric precursors. A prominent group of biocompatible cryogels for various biomedical and biotechnological applications can be obtained from such macromolecular precursors as proteins. Easily available and non-toxic bovine serum albumin (BSA) may act as precursor for the synthesis of cryogels both under action of exogenous cross-linking agent, or without it. Examples of albumin-based cryogels obtained in presence of denaturing agent and various thiols are known and more insights into the chemistry leading to formation of 3D-gel network of such cryogels is required to gain tools to precisely tailor the properties of such materials.

In the present study it was shown that consecutive freezing, frozen-storage [-15… -20°C] and thawing of BSA aqueous solutions with additions of denaturant (urea) and thiol-bearing reductant (cysteine) lead to the formation of covalent cross-links between the almost denatured polypeptide chains of albumin. It is showed that crosslinking is triggered by the reactions of thiol-disulfide exchange leading to evolving intermolecular disulfide bridges. Hydrophobic interactions pay significant role in the formation of 3D network of such BSA-cryogels. The resultant spongy cryogels have wide-pore morphology, and depending on the tempearaure at which cryogelation been processed, the size of gross pores varies from ~50 to ~150 μm. The optimum conditions for the preparation of such BSA-based cryogels were found to be as follows: [BSA] = 3-5 g/dL, [urea] = 0.5-2.0 mol/L, [Cys] = 0.01 mol/L, freezing temperature – within the diapason from -15 to -20°C. Thus prepared BSA-cryogels were demonstrated to be highly promising materials for biomedical application and can be potentially employed as sponge-like drug-release forms of various antibiotics, as well as scaffolds for 3D-cell culturing.
Aliphatic-aromatic polyamides – polyamides containing aromatic rings in acid and amine fragments macromolecular chain. Such polymers are prepared by various methods, including reaction molding. These include the gas-liquid polycondensation – heteropolycondensation of dichloroanhydride aromatic dicarboxylic acid and aliphatic diamine. From a technological point of view and in terms of physical and chemical properties of the final product preferably used in the gas phase phthalic acid dichlorides and the aqueous phase – hexamethylenediamine. The carrier vapor – air.

In the gas-liquid polycondensation pilot plant is obtained polymer based on terephthaloyl chloride and 1,6-diaminohexane – polyamide-6T:

\[
\begin{align*}
\text{n NH}_2(\text{CH}_2)_6\text{NH}_2 + \text{n Cl}^+\text{Cl}^- \quad \text{+ 2n NaOH} \\
\text{NaCl} \quad \text{2n H}_2\text{O}
\end{align*}
\]

The process is carried out at the liquid-gas from liquid phase at a section of its depth defined by the hydrodynamic conditions and the temperature of the reaction zone and the physical and chemical properties and acylatable acylating monomers.

A fundamental condition for the realization of the process is the formation of the mechanism of instant reaction gelled polyamide film, while the impact on it of shear stress. To make the fiber-film-polymer binder developed surface of the molding process they should occur in a mobile foam mode.

Commercially available terephthaloyl chloride contains 0.2% free carboxyl groups which initiate the process of formation polyanhydrides at temperatures above 110 °C with an excess of the chloride anhydrides. Products of this process accumulate in reactor-fibriderator and adversely affect its operation. To prevent this hexachloride-p-xylol was used.

\[
\begin{align*}
\text{Cl}_3\text{C}^-\text{CCl}_3^+ \quad \text{HO-C}=\text{C-OH} \\
\rightarrow 2 \text{Cl-C}=\text{C-Cl} + 2 \text{HCl}
\end{align*}
\]

Obtained polyamide was analyzed for the reduced viscosity (molecular weight), moisture content, water retention capacity. Using derivatograph «Termoscan-2» the temperature indicators of phase transitions is researched.
INTERACTION OF POLY-N-VINYLCAPROLACTAM (PVCL) MATRIX AND TITANIA NANOPARTICLES (NT) IN NT/PVCL COMPOSITES

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Preparation and studying of the composite materials consisting of a polymer matrix and a nanoscale inorganic phase as functional particles is a promising and rapidly developing scientific direction in the field of material science. Inorganic nanoparticles and a polymer carriers exert influence on each other, that results in new properties both nanoparticles and polymers as a part of nanocomposites, and nanocomposites.

The aim of the present study was to establish an interaction of a poly-N-vinylcaprolactam matrix (PVCL) and the titania nanoparticles (NT) at formation of NT/PVCL nanocomposites. NT/PVCL nanocomposites were prepared by three methods: mechanical trituration (method 1) (powders), physical precipitation (method 2) (films) and mechanical activation by ball-milling (method 3) (powders) of PVCL differing in drying temperature of aqueous PVCL solution (PVCL25, PVCL40, PVCL90) and NT (commercial Hombifine N and Hombikat UV100 with anatase, Degussa P25 – mixture of anatase and rutile in the ratio ~85%:15%); the samples prepared by us with anatase and η-phase.

According to wide angle X-ray scattering and IR spectroscopy it is established that the content of water in PVCL is antysymbatic correlates with the average size of a near ordered region of PVCL, which it is less in PVCL40. The results of small angle X-ray scattering indicate that the size of PVCL40 nanoparticles is also significantly less than PVCL25 ones, which increases upon transition from mechanically, ground PVCL40 to mechanoactivated. It is found that conditions of Hombifine N/PVCL preparation (method 3) affect on the size of nanoparticles: the duration and speed of a mechanical ball-milling are less, the size of nanoparticles is less.

Synthesis of nanocomposites by methods 1 and 3 leads to different changes in the NT:PVCL system (PVCL: various types of mechanical cracking, hydration and dehydration; NT: hydration and dehydration, phase and polymorphic transitions, changes of crystallinity degree). It is shown–that the nature of PVCL and NT, a method and conditions of nanocomposites preparation, a ratio of NT:PVCL bring an originality to the observed phenomena.

Synthesis of nanocomposites by physical precipitation (method 2) allows to stabilize NT in aqueous solution. Increasing of hydrodynamic diameter of NT particles in the solution leads to increasing of particle sizes and decreasing of crystallite sizes in solid state.

The highest degree of polymer capture for different modifications NT (method 2) was revealed by UV-spectroscopy for Degussa P25 (more than 98%) with the lowest ζ-potential (on an absolute value) of particles in comparison with other NT that indicates small stability of Degussa P25 particles in aqueous solution.

It is established that Hombifine N/PVCL nanocomposites obtained by method 2 show higher catalytic activity in decomposition of dye methyl orange under the influence of UV-radiation in comparasion with the nanocomposites synthesized by methods 1 and 3 and initial Hombifine N and PVCL. Bacteriostatic properties concerning microorganisms of Staphylococcus aureus, Escherichia coli, Candida albicans are found only for NT-anatas, η-phase.
THE OPPORTUNITY TO IMPROVE A BONDING STRENGTH OF A CARCASS RUBBER TO A TEXTILE CORD


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Rubber-cord parts and their goods are widely used in the technics and different fields of industry. Therefore, strength properties of adhesive compounds are of considerable importance.

A formation of the adhesive compound begins from its elements contact, at that, there is a wetting and spreading of the adhesive on the substrate’s surface, that helps to form the molecular contact. Dispersion forces with the formation of other molecular bonds act in the area of contact between molecules of the adhesive and substrate. Chemical bonds are formed due to the molecular contact under the action of heat in the presence of functional groups, capable to reactions with the substrate’s functional groups, in the adhesive’s elastomeric matrix. A viscose cord refers to the class of textile materials. It is prepared from artificial fibers. A cellulose serves as a material for the fibers. Physical-mechanical qualities of the viscose cord are higher than of a cotton cord. Thus, in comparison with the cotton, the viscose cord has more evenness of the thread, less decrease of the strength at the increase in temperature, less hysteresis losses, better resistance to repeated deformations, less heat build-up at a tire operation.

The maximum effect to increase the bonding strength in MEAPAN introduction is achieved in the dosage of 5,0 mass parts. Apparently, the chemical bonds formed at the interaction of MEAPAN and elastomer macromolecules are relatively stable.

The partial substitution of the resin to MEAPAN causes the positive influence on the bonding strength of the rubbers with fibers. The bonding strength of the rubbers with the viscose cord, treated by the impregnating composition with MEAPAN at 150°C is 30% higher, than with the viscose cord, treated by the common impregnating composition. It was mentioned earlier that the highest strength properties of the rubbers and rubber-cord systems are achieved in formation of a spectrum of vulcanization and interphase bonds of different energy. Apparently, often observed synergistic effect using surfactants with different types of functional groups, as well as in combination of products, improving wetting of the substrate by the rubber mixture and fluidity of the mixture with compounds forming the chemical bonds can be explained similarly.
APPLICATION OF TENGIZ SULFUR IN THE PREPARATION OF TECHNICAL RUBBERS
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In the process of cleaning crude oil from TCO of hydrogen sulfide produces elemental sulfur, which is in Tengiz to the results of the processing of "sour" oil and gas, indicating the content of hydrogen sulfide. Sulfur is the main vulcanization agent for most rubber products, including tires. To its quality and chemical composition subject to special requirements, which primarily include a high degree of purity of the product (minimum content of harmful impurities – metals of variable valence) and a high degree of dispersion. These characteristics determine the sulfur vulcanizing activity, the dispersibility in rubber, technical and technological properties of rubber mixes and rubbers.

The ever-increasing demands on the quality of the tyres would require the establishment of effective components of rubber compounds. Particular attention is paid to the development of curing agents. Back in the early 80-ies of the last century there appeared a polymeric sulfur, which quickly began to be applied in companies producing tyres and rubber products.

We have conducted research and this paper presents the results of experiments on the possibility of applying the purified polymer sulfur derived from the oil refining waste oil. Polymeric sulfur can reduce the amount of sulfur in the formulation without reducing the speed of vulcanization, which leads, ultimately, to improve the quality of rubber. The use of polymeric sulfur also allows the ability to adjust the elastic properties of the resulting rubbers. In the rubber mixture sulfur polymer was injected for partial or total replacement of ordinary sulfur. Polymeric sulfur was injected on laboratory rollers at the end of mixing, in the second stage, in order to prevent premature vulcanization. The experiments showed that the technology of mixing, processing of rubber mixtures and vulcanization is virtually indistinguishable from the standard mode as specified in technical specifications. The vulcanization of the samples was carried out at a temperature 1550°C for 15 minutes. The test samples for aging were carried out in an autoclave at a temperature of 393 K in an environment of saturated steam at a pressure of 0.2 MPa for 40 hours, and in similar conditions, under constant irrigation with 5% aqueous NaCl solution for 8 hours.

The results showed that the application of Tengiz sulfur leads to the increase of the strength properties of the belt and the tread rubber due to the increasing number of intermolecular bonds in lasternas the matrix, so the spacecraft all used in the compounding of sulfur reacts. Thus, the use of Tengiz sulfur will reduce the environmental burden on the environment and improve the quality of tyre rubbers.
DEVELOPMENT OF NANOSTRUCTURED CATALYSTS IMMOBILIZED ON THE GRAPHITE SUPPORTS FOR SYNTHESIS OF NOVEL HIGH-PERFORMANCE POLYOLEFINS

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The general purpose of this work is to develop novel type of the supported catalysts for olefin polymerization and co-polymerization giving high-performance polymers. Though synthesis of the commonly used supported Ziegler-Natta olefin polymerization catalysts is achieved usually via immobilization of suitable organometallic precursor on pre-treated (by organoaluminium compounds) calcinated silica-gel (or similar) surface, this work aims at the development of novel catalysts based on chemoselective sorption of the organometallic compounds bearing pi-ligands on porous graphite surface followed by treatment of thus obtained neutral surface organometallic species with suitable activator, such as organoaluminium or perfluorophenylboron compounds, to generate the required cationic complexes of importance for the producing olefin polymerization reaction. This protocol lead us to the development of highly active supported catalysts giving high-performane polyolefins of unusual microstructure and properties.

First, useful and convenient metal catalyzed cross-coupling protocols of importance for high-throughput synthesis of the required libraries organometallic pre-catalysts has been developed. Thus, using this methodology enabled us to synthesize dozens of required metal complexes in very timely manner. Then, we tested these pre-catalysts under different activation conditions using high-throughput olefin polymerization protocols. Again, this advanced methodology and dedicated equipment to faster the research was used to find hits among the studied homogeneous catalyst series. This work also required preliminary polyolefin characterization to obtain valuable rough information about performance of the catalysts under investigation. After the precise analysis of the obtained results selection of the most promising organometallic precursors to be used on the following step was done. Simultaneously, the detailed study of these and other organometallic derivatives of Group IV metals by HPLC technique using analytical Hypercarb column was carried out. This part of work aimed to model sorption of the complexes under investigation on the graphite support surface to understand mechanism of this sorption in more details. Thus, the second key parameter for the required selection of the most promising pre-catalyst targets was observation of irreversible retention of the complexes on Hypercarb column that made possible similar irreversible sorption of the complexes on surface of the graphite support during pre-catalyst immobilization. Thus obtained supported catalysts were studied in details in olefin polymerization and co-polymerization in order to find better conditions to obtain high performance polymer samples. Further on, microstructure and composition of the polymer samples obtained was studied in detail. Various dedicated protocols and approaches were used for this purpose including multidimensional chromatography techniques, advanced spectroscopic techniques as well as fractionations of polymers by composition and molar mass at high temperatures. Finally, major relationships between polymer microstructures (properties) and catalyst structure (composition)/polymerization conditions were elucidated. Thus, novel family of patentable supported olefin polymerization catalysts giving polyolefins having the improved functional properties was successfully developed and studied in detail.

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Nowadays strict environmentally friendly demands are made on plasticizable compounds while producing polyvinylchloride polymeric materials used in everyday life. One of the innovative solutions to this issue is to use renewable materials.

Trialkyl- and acetyltrialkyl citrates are well-known plasticizable citric acid-based compounds, which, due to their non-toxic plasticizer being, can substitute phthalic acid ester in many polymeric products which have a contact with foods, kids toys, medical instruments. The main task is to find an optimal technological solution to produce the above-mentioned articles, to prove their competitiveness with the conventional petrochemical-based plasticizers.

According to the literary information, the synthesis of the specified products consists of 2 steps: the citric acid-based esterification in the presence of acid catalysts with the preparation of trialkyl citrate and their acylation to acetyltrialkyl citrate as a result.

During the performance we investigated the reaction kinetics of the citric acid esterification conducted with low molecular weight alcohol C-C in the presence of three different catalysts: sulphuric, orthophosphoric, p-toluenesulphoric acid. Catalysts order of a reaction speed constants and activation energy in the range 70-110 °C are estimated. Activation barrier is shown to depend on the catalyst type and substratum structure.

On the base of the test data kinetic models of the processes we studied are proposed. The time needed to achieve 95% citric acid conversion in the esterification reaction is estimated. For instance, to produce trialkyl citrate at a temperature of 123 °C it takes from 1.5 to 5.2 hours, depending on the catalyst.

Laboratory specimens of acetyltributyl- and acetyltripentyl citrates are obtained. Their basic physical and chemical properties (density, chromaticity, acid number, saponification value, flash-point) are defined and compared to the properties of the widely used in the industry at present phthalic acid-based plasticizer – 2-dioctyl phthalate. Citric acid-based plasticizers are determined to surpass phthalate plasticizers in properties.
TENSILE STRESS RELAXATION IN A POLYMER-PLASTICIZER SYSTEM

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It seems that the most objective criterion to evaluate the plasticization impact on the
tensile stress relaxation process could be the absolute value of the relaxing stress part. Research
results of the relaxing stress part absolute value dependence on the plasticizer concentration
show that at the same initial stress equal to 28 MPa relaxing stress part increases almost linearly
with the plasticizer concentration increase, because the conditional equilibrium stress decreases
at a much faster rate than the initial one. At diethyl phthalate concentrations up to about 7%, the
relaxing stress part change just the same way at the initial deformation equal to 4%. However, at
concentrations above 7% the absolute value of relaxing stress part remains almost constant at the
initial deformation of 4%.

This effect may be yet another illustration of the point that at low concentrations
plasticizer plays a significant role in the sample structure formation. Consequently, at the equal
initial deformation, stress changes little with a slight diethyl phthalate concentration increase,
while the conventionally equilibrium stress decreases naturally. As a result, the absolute value of
the relaxing stress part increases. With further plasticizer's concentration increase, the initial
stress decrease due to the plasticizer concentration increase in the equal initial deformation mode
is offset by the conventionally equilibrium stress reduction of the same magnitude, while the
absolute value of relaxing stress part remains practically unchanged. Plasticization relaxation
mechanism is also revealed through the test temperature rise, as in the case of deformation until
the specimen fractures, is identical to the plasticizer's concentration increase.
CASCADE SYNTHESIS OF OLIGOORGANOSILSESQUIOXANES AND MULTIBLOCK SILOXANE COPOLYMERS AT NON-AQUEOUS MEDIA

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The siloxane block copolymers (BCP) of cyclolinear structure, containing alternate linear oligosiloxane "flexible" and polycyclic silsesquioxane "hard" blocks have valuable properties, including improved mechanical properties, thermooxidative stability, radiation resistance, high gas permeability and so on [1, 2].

Because of that, the BCP are of interest to create a composite polymer-of polymeric composite materials having valuable technical and performance properties.

The structure of the BSP macromolecules described by the general formula:

\[ \{ (\sim \text{Me}_2\text{SiO}\sim) \}_n [\text{RSiO}_{1.5}]_{m-a} [\text{RSi(O)OH}]_a \] \[ x \]

where R = Me; Et; Ph

We have developed the synthesis of BCP by hydrolytic polycondensation (HPC) of organotrichlorosilanes RSiCl3 with linear diorganosiloxanes, having a functional Si-Cl group at the ends of linear chains. The HPC proceed as a cascade-process.

Reactions were carried out at non-aqueous media in multi-component system comprising, along with organosilicone reagents and inert organic solvent(s), also carbamide and ketones.

A feature of these reaction systems is the fact that the water, required for the hydrolysis of organosilicon reagents, generated during the dehydro-condensation of carbamide with the ketones [3].

Under these conditions the structure of BCP macromolecules formed, containing alternate linear and polycyclic blocks. It appeared also, that this system is applicable for the preparation of soluble BCP containing methylsilsesquioxane as rigid blocks.

Effect of of various factors on the yield and composition of obtained BCP were studied. The structure, composition and polydispersity of BCPs were studied by \(^1\text{H NMR, }^{29}\text{Si -}\) spectroscopy, elemental analysis and GPC. A morphology of crosslinked BCP- samples (for R = Ph; Me) was studied by AFM and SEM.

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**References:**

Polyethylene terephthalate (PET) is difficult thermoplastic polyester of terephthalic acid and ethylene glycol. The fibers of PET are used for reinforcement of transmission belts and hoses, packaging tapes, and automotive airbags and are used in biomedical developments. The polymer is practically insoluble in water, and it has density of 1.4 g/cm³, melting temperature more than 250°C.

For obtaining PET fibers are used method electrospinning, which leads to the formation of fibers by electrostatic forces under electric field on a charged jet of polymer solution.

For this polymer was chosen solvent hexafluoroisopropanol (HFIP) with a purity > 99% and density 1.6 g/cm³.

In studying of the rheological property of solution PET in HFIP (dependence of viscosity on shear rate), it was established that the polymer concentration should be more than 5% for obtaining thin and strong fibers. In research were used solution with concentration of 6%, 9%, 12%.

For the selection electrospinning parameters, conductivity of the solution is an important characteristic. In the experiment applied voltage directly proportional to conductivity. If necessary to increase electrical conductivity for removal defects fibers (pears, beads), we used additive – tetrabutylammonium iodide. In our experiment, electrical conductivity ranged from 2.5 to 120 μS/cm.

Due to the decrease in the concentration decreases the radius of the obtained fibers (depending on the root). However, when concentration reaches the lower limit, which is determined from the rheological properties of the solution, electrospinning process can turn into the electrospraying process.

The applied stabilizes the electrospinning process. For this solution, we choose is the minimum voltage so that it supported the jet static. When the flow rate increases, the resulting fiber diameter increases. The capillary-to-collector distance affects the gluing degree (density) of the obtained material.

For obtain fiber structure of polymer solution were used parameters formation such us voltage in range from 9 to 40 kV, distance from the capillary to the collecting electrode 20 – 40 cm, polymer flow rate from 0.2 to 1.0 ml/h.

During the experiment, materials were obtained with diameter of fibers to 0.15 to 2 microns, with varying packing density and different pore diameters. The resulting materials can be used for purification of gas environments from aerosols in wide range of size.

The distribution of the sample diameter (solution 9% PET + HFIP).
GAMMA RADIATION INDUCED SYNTHESIS OF BACTERICIDAL NANOMATERIALS BASED ON CHITIN DERIVATIVE AND SILVER NANOPARTICLES

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Unique electrophysical, catalytic, and other properties of metal–polymer nanocomposite materials determine the interest of researchers to develop methods of synthesis of metal nanoparticles immediately within the polymer matrix [1]. Macromolecular compounds, in particular chitin derivatives, cannot only behave as stabilizers of resulting metal nanoparticles but also directly participate in the process of nanoparticle formation and act as a polymer matrix that control the size and shape of nanoparticles.

It has been demonstrated that in the process of gamma-induced reduction of Ag⁺ in the water solution of biodegradable carboxymethyl chitin polyelectrolyte a metal-polymer colloidal solution is formed, wherein the silver nanoparticles have a spherical shape and a size of about 1–5 nm. By using UV–Vis spectroscopy and transmission electron microscopy (TEM) the influence of carboxymethyl chitin concentration and radiation doses on the formation of clusters and silver nanoparticles in the metal-polymer colloidal solution has been observed. Silver nanoparticles colloidal solutions in carboxymethyl chitin exhibit clear concentration-dependent bactericidal activity towards the strains of gram-positive Staphilococcus aureus as well as gram-negative Salmonella typhimurium bacteria [2].

The obtained new macromolecular nanosystems can be used as antibacterial medium, in particular, in designing bactericidal liquid plasters, as a component for materials for bone tissue restoration in reparative medicine, and in electronics and optoelectronic applications (conducting ink).

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References:
One of the most important tasks of mechanical engineering is knowledge of the economic and institutional factors, which account is a prerequisite under pressure aided design and manufacturing technology of forming mold parts of casting in order to reduce its terms, facilitate the work of designers and engineers. For this days, we're widely using integrated system of computer-aided design and technological preparation of production, which makes it possible to automate routine tasks of designing and documentation for particular variant of the process adopted.

Exploration exposed the obturator oxygen mask. Used to improve the reliability of protection of the pilot, flying at high altitude and supersonic speeds, in an emergency depressurization of the cabin, under the influence of overloads and protection against exposure to air flow during ejection. The oxygen mask comprises a rigid frame made from the nasal cavity, the front side, bottom side, with the mounting surface for the exhalation valves, windows, systems fixing a mask to a protective helmet and inhalation valve, hose and tube, compensating tension. An obturator positioned within the frame.

Due to the additional requirements and complains from the pilots, the new material has been picked up. Than the mold was designed. Made the necessary studies, using a computer modeling.

The results of this work are:
1) Obtain geometrically regular parts, corresponding to the model and drawings with the given appearance. Finished part requires minimal rework.
2) Mastered the manufacture of molds of the complex parts on modern technology, which allows to provide the required accuracy and appearance.
3) The maximum reduced labor input.

The product obtained, passed the technical control department.

References:
POLYMER COMPOSITIONS FOR PREPARATION OF CHEMICALLY PURE, HIGH-POROUS SiC CERAMICS


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2Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, Russia

Dynamic development of engineering industry can be made only through application of modern materials and manufacturing technologies. Silicon carbide is one of the main components of high-temperature ceramics differentl-purpose designation. Polymer technology [1] meets the severe requirements on purity of silicon carbide, and allows obtaining silicon carbide as articles of complex shape with preset porosity. This work is devoted to the preparation of chemically pure silicon carbide from polymer composite materials (PCM) based on phenol-formaldehyde binder and silicon dioxide using non-woven fabric (made from quartz fibers) wastes as starting materials.

The formulation of polymer composite material based on phenol-formaldehyde binder and quartz fiber scrap as well as the technology for the preparation of high-porous & high-strength ceramics were developed. The influence of filler preparation modes on properties and composition of articles from polymer and carbon-based composite materials was studied. It was shown that preliminary thermal treatment and removal of organic products from quartz fibers were not needed. The influence of time and temperature on synthetic conditions, structure, composition and properties of silicon carbide was investigated. Optimization of composition and manufacturing technology of PCM allowed obtaining chemically pure silicon carbide as bulk ceramics with the following properties: porosity of 82-88%, ultimate compressive strength of 2.4-10 MPa.

Acknowledgements

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