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Синтез смешанных оксидов никеля и алюминия и исследование их катализитической активности

В работе исследован фазовый состав и структура смешанного оксида полученного из слоистого двойного гидроксида Ni-Al (Ni:Al = 3:1). Гидроксид, полученный путем осаждения нитратов никеля и алюминия, обладает гексагональной кристаллической решеткой с размерами кристаллитов 7 нм. После прокаливания гидроксида при температуре 500 °C размер кристаллитов оксида Ni-Al составил 4 нм. Они состоят из октаэдрических слоев и незначительного количества шпинельной структуры. В продуктах крекинга н-алканов в присутствии полученного смешанного оксида Ni-Al увеличивается содержание их низкокипящих гомологов, образуются алканы разветвленной структуры.

Ключевые слова: слоистый двойной гидроксид Ni-Al, термический анализ, смешанный оксид Ni-Al, рентгеноструктурный анализ, н-алканы, каталитический крекинг, газовая хроматография, хромато-масс-спектрометрия.

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Synthesis of Ni-Al Mixed Oxides and Study on Their Catalytic Activity

In this work, the phase composition and structure of a mixed oxide of a layered double hydroxide, which is based on Ni-Al, were investigated (Ni:Al = 3 : 1). The hydroxide obtained by precipitation of nitrates of Ni and Al has a hexagonal crystal lattice with a crystallite size of 7 nm. After calcination of the hydroxide at a temperature of 500°C, the size of the crystallites of Ni-Al oxide was 4 nm, consisting of octahedral and insignificant number of spinel layers. In the products of cracking of n-alkanes in the presence of the mixed oxide Ni-Al, the content of their low-boiling homologs increases, and alkanes with a branched structure are formed.

Key words: Ni-Al layered double hydroxide, thermal analysis, Ni-Al mixed oxide, X-ray analysis, n-alkanes, catalytic cracking, gas chromatography, chromatography-mass spectrometry.

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Изомеризация н-гексана на никелевых катализаторах, нанесенных на модифицированный монтмориллонит

Приготовлены различными методами никелевые катализаторы, нанесенные на активированный монтмориллонит, модифицированный оксидом титана и морденитом и изучены их катализитические свойства в реакции изомеризации н-гексана. Максимальная конверсия н-гексана, равная 36,2%, достигнута на никелевом катализаторе, нанесенном на активированный монтмориллонит и модифицированный морденитом и TiO₂, введенных путем смешения компонентов. При оптимальном составе катализатора

при 350°C и 1 атм. из н-гексана образуются изомеры C₄–C₇ с выходом 34,2% и селективностью 93,6%. Показано, что такой состав катализатора из числа исследованных характеризуется максимальными удельной поверхностью, количеством мезопор, суммарным содержанием слабых и средних по силе кислотных центров.

Ключевые слова: никелевые катализаторы, н-гексан, изомеризация, монтмориллонит, оксид титана, морденит.

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Isomerization of n-Hexane on Ni Catalysts Supported on Modified Montmorillonite

The properties of Ni catalysts supported on activated montmorillonite modified by TiO₂ and mordenite, as well as their catalytic properties in the n-hexane isomerization reaction, were studied by various methods. The maximum conversion of n-hexane, equal to 36.2%, was found on a Ni catalyst supported on activated NaHMM and modified by mordenite and TiO₂, introduced by mixing the components. At the optimal composition of catalyst Ni/NaHMM + TiO₂ + HM at 350 °C and 1 atm. C₄–C₇ isomers are formed from n-hexane with a yield of 34.2% and a selectivity of 93.6%. It has been shown that this catalyst composition among those studied is characterized by the maximum specific surface area, the number of mesopores, and the total amount of weak and medium strength acid sites.

Key words: Ni-catalysts, n-hexane, isomerization, montmorillonite, titanium oxide, mordenite.

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Исследование взаимного влияния противоизносных и противозадирных присадок на характер износа поверхности металла

Установлена особенность взаимного влияния аминофосфатных противоизносных присадок и противозадирных присадок, содержащих полисульфидные группы, на степень и характер износа и задира трущихся поверхностей. Показана невозможность получить высокий уровень противоизносных и противозадирных свойств при одновременном использовании указанных присадок для получения трансмиссионного масла из масел вторичной переработки. Предложено решение этой проблемы введением дополнительной присадки умеренной активности. Методами растровой электронной микроскопии и энергодисперсионного рентгеноспектрального микроанализа выявлено наличие фосфора на поверхности металла при нагрузках, близких нагрузке сваривания, и отсутствие фосфора на поверхности металла при умеренных нагрузках. Высказано предположение, что при высоких нагрузках, вследствие высокой активности аминофосфатов к поверхности металла, происходит конкурентное формирование фосфатной пленки, которая мешает образованию защитного серосодержащего слоя за счет противозадирной присадки.

Ключевые слова: аминофосфатные противоизносные присадки, противозадирные полисульфидные присадки, конкурентная адсорбция, антагонистическое влияние, масла вторичной переработки, трансмиссионные масла.

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Investigation of the Mutual Influence of Antiwear and Extreme Pressure Additives on the Nature of Metal Surface Wear

The peculiarity of the mutual influence of aminophosphate antiwear additives and extreme pressure additives containing polysulfide groups on the degree and nature of wear and scuffing of friction surfaces is established. It is shown that it is impossible to obtain a high level of antiwear and extreme pressure properties while using these additives to produce gear oil from recycled oils. The solution of the problem is proposed by introducing an additional additive of moderate activity. By the methods of scanning electron microscopy and energy dispersive x-ray spectral microanalysis, the presence of phosphorus on the surface of the metal at loads close to the welding load was revealed, and the absence of phosphorus on the metal surface at moderate loads. It is suggested that at high loads, due to the high activity of aminophosphates to the surface of the metal, there is a competitive formation of a phosphate film, which prevents the formation of a protective sulfur-containing layer due to an extreme pressure additive.

Key words: aminophosphate antiwear additives, extreme pressure polysulfide additives, competitive adsorption, antagonistic effect, secondary processing oils, gear oils.

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Определение содержания антиокислительной присадки и продуктов ее разрушения в работающих моторных маслах

В процессе окисления моторного масла под действием высоких температур образуются сернистые соединения, и определить остаточное содержание активной присадки является достаточно сложной задачей. Для определения присадки ДФ-11 масло М-10Г2к окислялось в термостате. Установлено, что при длительности окисления 8 и 10 ч по потенциометрической кривой титрования можно определить лишь количество меркаптановой серы. Для полного определения серосодержащих соединений в окисленном масле предложен алгоритм и методы их определения, что в условиях эксплуатации позволяет прогнозировать износ и срок службы смазочного масла.

Ключевые слова: моторное масло, присадка, окисление, разрушение, сернистые соединения, оптическая плотность.

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Determination of the Content of Antioxidation Additive and Products of Its Destruction in Working Engine Oils

In the process of oxidation of motor oil under the action of high temperatures, sulfur compounds are formed, and it is rather difficult to determine the residual content of the active additive. To determine the additive DF-11, oil M-10G2k was oxidized in a thermostat. It has been established that with the oxidation time of 8 and 10 hours, only the amount of mercaptan sulfur can be determined from the potentiometric titration curve. For a complete determination of sulfur-containing compounds in oxidized oil, an algorithm and methods for their determination are proposed, which, under operating conditions, makes it possible to predict the wear and service life of lubricating oil.

Key words: engine oil, additive, oxidation, destruction, sulfur compounds, optical density.

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Регулирование реологических свойств дисперсных систем для обеспечения современных требований к нефтяным дорожным битумам

Разработана рецептура сырья для производства дорожных битумов на основе тяжелых остатков нефти Арланского месторождения. Применяемые научно-технологические решения, включающие направленное регулирование фракционного и группового химического состава гудрона арланской нефти при смешении с регулирующими эти составы компонентами-полупродуктами, позволяют получать дорожные вязущие материалы, соответствующие современным требованиям дорожно-строительной отрасли.

Показано, что применение арланского гудрона в составе битумного сырья является экономически и технологически обоснованным, так как позволяет высвобождать значительные объемы остатков западносибирской нефти с целью переработки их в высококачественный кокс, а содержащиеся в арланском гудроне смолисто-асфальтеновые вещества обеспечивают высокую долговечность получаемых дорожных битумных вязущих материалов.

Ключевые слова: нефтяная дисперсная система, арланский гудрон, западносибирский гудрон, дорожные битумы, реологические свойства, фракционный и групповой химический состав.

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Regulation of Rheological Properties of Raw Materials as Way of Providing Modern Requirements to Road Bitumens

Recipes of raw materials for production of road bitumen on the basis of Arlan oil field are developed. There is a directional effect on disperse systems that modifies the group chemical composition of the heavy residues Arlan oil field when they are mixed with plasticizing tar with companion intermediates. This is what makes it possible to obtain road binder materials that meet modern requirements of the road construction industry. Oxidation of bituminous raw materials on the basis of Arlan oil allows obtaining road binder materials with high cohesion and resistance to aging.

From the point of view of the production of road bitumen, the results obtained allow us to affirm the optimality of the chosen approach for regulating the rheological properties of heavy tar, the suitability of the developed technological solutions for the production of road bitumen, and the high potential of oil dispersed systems (residues of heavy Arlan crude processing). The use of bituminous raw materials, based on Arlan oil, is economically and technologically sound, since it allows the release of significant amounts of residues of West Siberian oil for subsequent processing into high-quality chark. Heavy aromatic compounds, resins and asphaltenes, contained in Arlan tar, ensure high durability of the road bituminous binders obtained.

Key words: *oil dispersed system, Arlan field, Arlan tar, West Siberian tar, road bitumen, rheological properties, group chemical composition.*

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Синтез и тестирование нового кинетического ингибитора гидратов метана на основе амфи菲尔ного полиуретана

Разработан кинетический ингибитор гидратообразования метана на основе амфи菲尔ного полиуретана. Эффективность ингибирующего действия нового реагента оценивалась в реакторе высокого давления с перемешиванием путём измерения времени начала гидратообразования и давления в системе. Результаты показывают отличную эффективность амфи菲尔ного полиуретана в увеличении времени индукции (в 15 раз) и снижении скорости роста гидратов (в 2,5 раза) по сравнению с системой с чистой водой. Кроме того, ингибитор на основе уретана не показал значительного роста гидратов метана после нуклеации.

Ключевые слова: гидратообразование, гидрат метана, кинетический ингибитор, полиуретан.

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Synthesis and Evaluation of New Kinetic Methane Hydrate Inhibitor on the Basis of Amphiphilic Polyurethane

In this work, we have developed new kinetic methane hydrate inhibitor based on amphiphilic polyurethane. The efficiency of the new reagent was evaluated in a high-pressure reactor with mixing by measuring the onset of hydrate formation time and the change of pressure in the system. The results show the excellent inhibition effect of amphiphilic polyurethane in increasing the induction time (15 times) and reducing the growth rate of hydrates (2.5 times) compared with a system with pure water. In addition, a urethane-based inhibitor did not show significant growth of methane hydrates after nucleation.

Key words: *gas hydrate formation, methane hydrate, kinetic inhibitor, polyurethane.*

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Использование диспергированного твердого вещества баженовской свиты

при разработке запасов легкой нефти

В условиях низкопроницаемой тюменской свиты попутный нефтяной газ и продукт внутрипластавовой трансформации воздуха близки по нефтьевые свойствам. Предложен новый подход к разработке запасов нефти тюменской и баженовской свит, заключающийся в том, что трансформацию воздуха в инертный газовый агент рекомендуется производить при окислении твердого органического вещества баженовской свиты, диспергированного в объеме породы, а не нефти. Одновременно при неравномерном прогреве породы баженовской свиты будет происходить образование искусственных трещин.

Ключевые слова: внутрипластавовая трансформация, воздух, окисление, пористая среда.

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The Use of Dispersed Solids of the Bazhenov Formation

in the Development of Light Oil Reserves

Associated petroleum gas (APG) and product of air in-situ transformation are similar in oil-displacing properties under the conditions of the low-permeable Tyumen Formation. A new approach to the development of oil reserves of the Tyumen and Bazhenov Formations is proposed. It consists in the fact that the transformation of air into an inert gas agent is recommended during the oxidation of the solid organic matter of the Bazhenov Formation dispersed in rock (not in oil). At the same time, the artificial cracks will form with uneven heating of rock of the Bazhenov Formation.

Key words: *in-situ transformation, air, oxidation, porous medium.*

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Thermal Stability Evaluation of Sodium Formate on Polymer drilling Fluids

The objective of this study is to investigate the profound impact of formate on the rheological characteristic of water based fluids by comparing two different laboratory measurement methods, dynamic HTHP rheological test and static hot roll aging test, respectively. The particular samples utilized in this study were polymer muds. Consequently, HTHP tests reflected that sodium formate has effectively retained the dynamic viscosity at HTHP conditions. Hot roll

experimental results indicated that sodium formate has performed the obviously impact on the rheological properties of polymer fluids at room temperature after heating. Moreover, filtration loss of polymer fluids with sodium formate displayed a slight increase compared with polymer itself but was obvious controlled. Both different tests method and results are showed that formate has the ability to maintain the property of polymer fluid on the HTHP conditions and determine that it is reasonable to use sodium formate as thermal stabilizer into polymer fluid.

Key words: *rheological properties, filtration loss, sodium formate, high temperature and high pressure test, hot rolling test.*

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Evaluation and Research on the Performance of Plug Anti-Gas Channeling Cementing Material

The slug anti-gas channeling technology is studied in this paper to optimize the micro-expansion slug anti-gas channeling material through laboratory tests with the help of the idea of outer pipe sealing, inject casing annulus with cement slurry, activate and solidify the casing annulus with temperature and other external conditions, and realize oil and gas sealing at low cost, so as to effectively solve the wellhead pressure problem.

Key words: *wellhead pressure, anti-gas channeling, outer seal, micro-expansion.*

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Modified Models for Prediction of Flash Point of Multi-component Mixtures in Air Compressor System during Air Injection LTO Process of Heavy Oil Reservoirs

Flash point acts as a significant safety indicator to evaluate the fire and explosion hazards of multi-component mixtures in air injection low-temperature oxidation (LTO) assisted with steam stimulation process of oilfield exploration and exploitation. In this work, a continuous experimental measurement of flash point of the multi-component mixtures in air compressor system is undertaken. Different theoretical models are compared with the experimental data and the comparative results reveal that the calculations by using traditional models have a certain deviation with the experimental data because of the effect of high vapor pressure on the flash point. For this reason, we modified and proposed a new model for predicting the flash point for multi-component mixtures under high pressure associated with UNIFAC consortium. The comparative result shows that the modified UNIFAC-based model proposed is able to represent well the experimental data over the entire composition range. One purpose of this study is to predict the flash point of multi-component mixtures in air compressor system under increasing pressure without experimental determinations. More importantly, it is hoped that this study can offer reference for hazards analysis of the air compressor system during air injection LTO process of heavy oil reservoirs.

Key words: *flash point, multi-component mixtures, air compressor, LTO, modified model.*

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Pressure Distribution of Oil-Water Seepage Based on Oil-Water Two-Phase Threshold Pressure Gradient

Given the status quo that the slow progress on the study of two-phase flow characteristics in low-permeability reservoirs based on the oil-water two-phase threshold pressure gradient, we select an oil-water two-phase threshold pressure gradient model by considering the uneven radial distribution of the water saturation in oil-water two-phase flow of low-permeability reservoirs. Then we use the oil-water relative permeability curves and the Buckley-Leverett equation to determine the oil-water mobility ratio and the functional relationship between the two-phase threshold pressure gradient, the oil saturation and the radial distance. Thus, we build a radial oil-water flow model based on the oil-water two-phase threshold pressure to deduce the pressure distribution equation. Results show that there is a linear relationship between the oil-water two-phase threshold pressure gradient and the oil saturation, while there is a quadric relationship between the oil-water two-phase mobility ratio and the oil saturation. The oil-water two-phase threshold pressure gradient in low-permeability reservoirs has a great influence on the formation pressure distribution. When considering the oil-water two-phase threshold pressure gradient, the formation pressure lower than that without considering, which is more intense in the near wellbore zone.

Key words: *low-permeability reservoir oil-water two phase threshold pressure gradient radial flow pressure distribution model.*

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Dynamic Analysis of Perforating Strings

Perforating operations increase effective productivity of oil and gas wells. Because the understanding of the characteristics and rules of the output characteristics of the perforated string in the complex downhole environment is not enough, the failure of the perforated string and the accident of the perforation explosion happen frequently. Therefore, it is very important to conduct further research in this field. In this paper, the dynamic response of perforation string is studied. Through a series of investigation and analysis, simplified static model load analysis and perforation column dynamics analysis, using ANSYS LS-DYNA software, conducted a series of targeted modeling and simulation calculations. Establish a simplified model of perforation string and analyze the mechanical response characteristics of the perforation string caused by different loads

Key words: *perforating, LS-DYNA, string, stress.*

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The Application of Artificial Fish Swarm Algorithm in the Optimization of Trajectory

In drilling field, many complex design of global optimization problem will appear, the complexity is multivariate, nonlinear, extreme value. This kind of problem is also difficulty in the optimization of trajectory. For the well trajectory optimization design and control, many scholars have designed many algorithms, but there are more or less defects. This paper takes the shortest length of the well as the target function and uses the artificial fish swarm algorithm and Matlab software to optimize trajectory. Then compare the results with the example in literature, the numerical results show that the artificial fish optimization algorithm can get the better parameters than that of literature, the well length is much shorter. This indicates the correctness and reliability of the algorithm.

The algorithm is simple in structure, convergence is much better and can quickly get an approximation global optimal solution, so artificial fish optimization algorithm can be used for the optimization design of trajectory.

Key words: *artificial fish swarm, well length, trajectory, optimization.*