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PREPARATION OF NANODISPERSED CALCIUM CARBONATE FOR THIXOTROPIC SYSTEMS BY THE CARBONATION METHOD

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A micellar model for the preparation of a nanodispersed carbonate core for thixotropic systems is proposed. According to this model, the carbonation process occurs in an inverted microemulsion system, where the internal dispersed phase – a water–methanol mixture containing calcium hydroxide – is integrated with the oil–toluene dispersion medium (petroleum or synthetic oils) into a unified system by a synthesized biosurfactant. This is followed by bubbling carbon dioxide through the calcium hydroxide-containing phase, resulting in the formation of a grease thickener that functions as an emulsifier-stabilizer. The resulting calcium carbonate crystallites exhibit ellipsoidal and spherical shapes, and include vaterite and calcite polymorphic modifications, with particle sizes ranging from 6–18 nm to 34–51 nm, as confirmed by X-ray diffraction, infrared spectroscopy, and scanning electron microscopy. The developed calcium-based grease compositions using the synthesized emulsifier-stabilizer demonstrate enhanced protective and tribological properties, as well as improved oxidative and colloidal stability. These greases are intended for lubricating friction units in machines and mechanical systems.

Keywords: synthesis, nanodispersed carbonate core, surfactant, thixotropic systems, grease composition.

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Introduction

Currently, researchers are paying increased attention to ultrafine nanoscale substances and compositions containing them. In contrast to macroscopic particles, they exhibit unique mechanical, chemical, electrical, optical, magnetic, electro-optical, and magneto-optical properties that have led to their use in catalysis, greases, ceramic and polymeric materials, and microelectronic devices [1].

Greases play an important role in the country's economy, as their main consumers are machine building, metallurgy, transport, agriculture, and other industries. The effectiveness of nanotechnology in producing lubricants is due to the high antioxidant and lubricating properties of lubricants stabilized by nanodispersed substances over a wide range of temperatures and loads. There are many ways to produce nanomaterials [1–5], but chemical methods are preferred, based mainly on the use of microemulsion systems, where reactions allow controlling particle size, morphology, and polymorphic modification.

In recent years, special attention has been paid to the carbonation process in inverted microemulsions due to the formation of nanodispersed substances in them as reactors, which give thixotropic systems effective performance properties. Such materials include dispersions of calcium carbonate stabilized with emulsifiers-stabilizers or grease thickeners (calcium alkyl sulfonates, alkyl salicylates, or alkyl phenolates), multipurpose high-temperature complex superalkaline greases with improved tribological properties and increased oxidation stability at high speeds and loads in aggressive environments [6]. However, due to the widespread use of such emulsifiers-stabilizers, there is a steady trend toward replacing petrochemical thickeners with alternative renewable natural substances [7,8].

Several lubricants with calcium thickeners are known [6,9–11]. In the metallurgical industry, greases [9,10] based on petroleum or synthetic oil, including calcium carbonate (calcium carbonate and calcium hydroxide) stabilized with superalkaline calcium sulfonate as a thickener, are still widely used. These greases are characterized by a high dripping point, as well as a good antioxidant and protective ability. As a result, they are recommended for use as an anti-corrosion coating for mechanisms operating at high temperatures and high humidity. However, due to its relatively low lubricating properties, this grease cannot be used as an antifriction grease. Another grease used is made based on residual petroleum oil and complex calcium soap of fatty and acetic acids and contains an antioxidant additive. In terms of antioxidant stability, protective properties, and tribological characteristics, especially at elevated temperatures, this grease does not meet the requirements of modern specifications for metallurgical greases [6]. Greases that use calcium soaps of fatty acids, and animal and vegetable triglycerides as thickeners are attracting attention, as they have a positive effect on the formation of the grease's structural framework, reduce penetration, increase colloidal stability and shear strength [11].

Therefore, it is important to synthesize calcium carbonate nanodispersions to improve the colloidal, antioxidant, and tribological properties of thixotropic systems. Nanodispersed calcium carbonate exists in crystalline modifications – calcite, aragonite, vaterite, and amorphous. The most stable of them is calcite, and the least stable is vaterite [1,2].

Thus, this work aims to develop a micellar model for the preparation of a nanodispersed carbonate core of thixotropic systems and the formation of a grease thickener based on alternative renewable natural raw materials for the development of grease compositions with improved performance characteristics.

Experimental

Materials

As a raw material for the synthesis of biosynthetic surfactants, propose to use secondary fatty raw materials: concentrated phosphatides (phosphatidic sludge) of vegetable oils. The physicochemical properties of this raw material are described in refs. [11–13]. Monoethanolamine (99.5%), toluene (99.5%), sodium carbonate (Na_2CO_3, 99.3%), calcium chloride ($CaCl_2$, 95.4%), calcium hydroxide ($Ca(OH)_2$, 99.1%), and carbon dioxide (CO_2, 99.0%) were purchased from Chemlaborreactiv *LLC (Ukraine)*.

Analytical methods

The phase identification of the products was performed by X-ray diffraction (XRD) method using a MiniFlex 300/600 diffractometer (Rigaku, Japan). The diffraction patterns were recorded using Cu-Kα radiation (λ=0.15418 nm), the operating voltage of 40 kV and a current of 15 mA. XRD pattern of samples was obtained in the 2θ range between 2^0 and 100^0 with a step of 0.02^0. The scanning electron microscopy (SEM) images were taken using Zeiss Evo-10 (Carl Zeiss Microscopy, USA) microscope working at 20.0 kV. The IR spectra of products were recorded on the surface of the diamond prism of the IR-spectrometer with Fourier transform Shimadzu IRAffinity-1Sn (Japan) with ATR-console Speacac GS 10801-B.

Samples of thixotropic systems were evaluated according to the following indicators penetration (ISO 2137), dropping point (ISO 2176), resistance to oxidation (state standard GOST 5734), tribological characteristics (state standard GOST 9490), and colloidal stability (state standard GOST 7142 method A).

Synthesis of a biosynthetic surfactant

Greases using a surfactant as an additive or thickener based on phosphatide concentrate with various additives or in a mixture with mineral and synthetic oils are characterized by effective tribological and viscosity characteristics. However, their use in most cases is complicated due to high chemical and thermal oxidation instability, as a result of the relatively high chemical activity of unsaturated bonds [11]. To eliminate unstable centers, the chemical transformation of oil and fat raw materials is carried out, which consists of nucleophilic substitution of carboxyl groups of glycerides near the C=O bond and/or addition via double bonds. All these transformations are accompanied by the destruction of the triglyceride structure or the introduction of new functional groups, which endows oleochemical products with several improved performance characteristics and expands the possibilities of their use in thixotropic systems.

The chemical modification of phosphatide concentrate is carried out by transamidation of fatty acids with monoethanolamine under the action of calcium hydroxide as a catalytic reagent in a nitrogen medium. Papers [12,13] describe the method for the synthesis of biosurfactants, investigate their properties, and prove their structure.

The synthesized biosynthetic surfactants have a grease-like consistency, brown in color, with a specific amine odor, a yield point of 30^0C, surface tension of 35–36 mN/m, and a density of 1014 kg/m^3.

Synthesis of nanodispersed calcium carbonate

The nanodispersed carbonate core of thixotropic systems was obtained by the carbonation method [9]. The carbonation process was carried out in a reactor equipped with a thermometer, a stirring device, a CO_2 supply tube, and a reflux condenser. The reaction vessel is connected to the atmosphere through a reflux condenser and a glycerine seal. Toluene was used as a hydrocarbon solvent and methanol as a promoter and conversion agent. As a dispersion medium, a base petroleum oil with a kinematic viscosity of 20.5 mm^2/s at 100^{0}C, a pour point of −18^{0}C, and a flash point of 240^{0}C was used.

Dissolved bio-surfactant in the hydrocarbon fraction (toluene, petroleum oil) was loaded into the reactor and an aqueous solution of methanol with calcium hydroxide was gradually added. The mixture was heated to 40^{0}C and stirred at 3000 rpm for 1−2 min. The method consists of further bubbling with carbon dioxide in the calcium hydroxide microemulsion system, namely, CO_2 was supplied to the system under intensive stirring. The carbonation process was terminated when the absorption of carbon dioxide by the reaction mass stopped and the pressure in the system increased. Then the hydrocarbon solvent and promoter were removed from the system, and the finished grease composition was heat and mechanically treated.

Samples of grease composition were obtained at a molar ratio of $Ca(OH)_2$:biosurfactant of 1:0.18 (sample 1), 1:0.27 (sample 2), and 1:0.36 (sample 3). The molar ratio of solvent:promoter for all samples was 1.4:1. For comparison, a sample of industrial calcium grease Uniol-2 (sample 4) according to GOST 23510 was used.

For the analysis of calcium carbonate crystallites, the selected samples 1, 2, and 3 were centrifuged, and the precipitated $CaCO_3$ particles were washed several times with ethyl alcohol and distilled water and dried at 80^{0}C for 3 hours.

Results and discussion

The carbonation method is one of the most common methods for the synthesis of calcium carbonate due to its low cost, high yield, and purity. A promising method for obtaining a nanodispersed carbonate core of thixotropic systems is the model according to which the carbonation process takes place in an inverted microemulsion, i.e., a system in which the internal dispersed phase, a water-methanol mixture with calcium hydroxide, is bound to the oil-toluene dispersion medium (petroleum or synthetic oils) into a single system by a biosynthetic surfactant, followed by bubbling of calcium hydroxide with carbon dioxide and formation of a thickener as a grease emulsifier-stabilizer. The thickener forms the structure that gives the grease its plasticity, strength, colloidal stability, and other volumetric and mechanical properties. Although the concentration of thickener in greases is relatively low, ranging from 3% to 30%, it is the thickener that primarily determines their performance characteristics [6,7,9].

As a result of the carbonation process, a nanodispersed carbonate nucleus was obtained in the dispersed phase of the microemulsion system of ellipsoidal and spherical forms, vaterite, and calcite polymorphic modification. The resulting $CaCO_3$ crystallites were analyzed by X-ray diffraction, infrared spectroscopy, and scanning electron microscopy.

For the targeted control of the size and morphology of carbonate particles, biosurfactants, and organic solvents were used, took into account into account the water:surfactant concentration ratio, the type, and concentration of reagents, the properties of the aqueous and hydrocarbon phases, etc. [6,14,15].

Biosurfactants adsorbed on the surface of hydrophilic carbonate particles allow obtaining products capable of dispersing in organic materials, and also reduce the free surface of $CaCO_3$ crystallites and thus limit its growth. The main factors that determine the self-organization of synthesized biosynthetic surfactants are the presence of hydrophilic polar functional groups (alkylolamide and oxyethyl) in biosurfactant molecules, which facilitates dispersion in water, while hydrophobic non-polar aliphatic chains of higher carboxylic acids give the biosurfactant molecule an affinity for organic solvents. In addition, the hydrophilic polar component of the biosurfactant molecule is calcium glycerol phosphatides, which act as a co-surfactant. The dispersed phase of micelles of this system is considered as micro/nanoreactors in which nanoparticles are formed. The hydrophilic polar functional groups are bound to water, methanol, and $Ca(OH)_2$, forming a bulk hydrophilic core, and the long hydrocarbon chains of C_9−C_{40} form an outer hydrophobic shell that reliably shields the polar part and ensures the affinity of the micelles for the hydrocarbon environment.

Organic solvents in the media affect the solubility of reaction products and the interaction between calcium carbonate crystallites. Calcium carbonate crystals synthesized in organic solvents are smaller than those obtained in an aqueous medium. The precipitated calcium carbonate synthesized in pure methanol or its aqueous solution is two times smaller than that obtained in aqueous medium [1].

X-ray phase analysis

Figure 1 shows the X-ray diffraction patterns of the sample's thixotropic systems at a molar ratio of

$Ca(OH)_2$:biosurfactant of 1:0.18 (Fig. 1a, sample 1), 1:0.27 (Fig. 1b, sample 2), and 1:0.36 (Fig. 1c, sample 3). In the X-ray diffraction pattern of the sample 1 (Fig. 1a), the fixed diffraction peaks at 25.14, 27.25, 32.89, 44.09, and 50.1^0 correspond to planes (100), (101), (102), (110), and (112) with a size of $CaCO_3$ crystallites from 6–15 nm to 28 nm of the vaterite modification of the ellipsoidal shape. In the X-ray diffraction pattern of the sample 2 (Fig. 1b), the fixed diffraction peaks at 25.01, 27.09, 32.92, 44.02, and 50.06^0 correspond to planes (020), (120), (211), (031), and (231) with a size of $CaCO_3$ crystallites from 6–18 nm to 34"51 nm of the calcite modification of the spherical shape. In the X-ray diffraction pattern of the sample 3 (Fig. 1c), the fixed diffraction peaks at 25.23, 27.28, 32.93, 44.21, and 50.11^0 correspond to planes (011), (111), (211), (002), and (202) with a size of $CaCO_3$ crystallites from 6–11 nm to 44 nm of the calcite modification of the spherical shape.

Infrared spectroscopy

The results of IR spectroscopy confirmed the formation of a nanodispersed carbonate core (Fig. 2). For the sample 1 (Fig. 2a), intense absorption bands in the region of 1412 cm^{-1}, 873 cm^{-1}, and 744 cm^{-1} are observed for the vaterite form of $CaCO_3$ crystallites. For the sample 2 (Fig. 2b) and sample 3 (Fig. 2c), intense absorption bands are recorded in the region of 1396 cm^{-1}, 872 cm^{-1} and 711 cm^{-1} typical of the calcite form of $CaCO_3$ crystallites.

Scanning electron microphotography (SEM)

A scanning electron micrograph (Fig. 3) illustrates the calcium carbonate crystallites. At a molar ratio of $Ca(OH)_2$:biosurfactant of 1:0.18 (Fig. 3a, sample 1), the vaterite polymorphic modification of calcium carbonate crystallites with an ellipsoidal shape is manifested. With an increase in the molar ratio of $Ca(OH)_2$:biosurfactant of 1:0.27 (Fig. 3b, sample 2) and 1:0.36 (Fig. 3c, sample 3), the vaterite polymorph transforms into spherical calcite. The results of the scanning electron micrograph images confirm the X-ray phase analysis and infrared spectroscopy data.

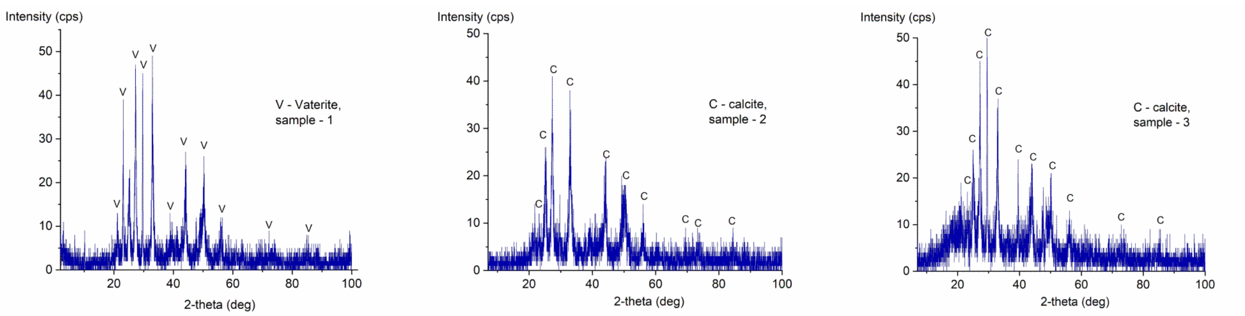
Properties of grease compositions based on nanodispersed calcium carbonate

A micellar model for the preparation of a nanodispersion carbonate core of thixotropic systems for the development of grease compositions with improved performance characteristics has been proposed (Table). The micelles of the thixotropic system in the friction zone, orienting themselves with the hydrophilic surface towards the metal surface or other hydrophilic friction surfaces, fill the smallest irregularities with nanodispersion calcium carbonate to form the strongest boundary films.

Table shows a comparative analysis of the quality indicators of the manufactured samples 1, 2, and 3 of calcium grease compositions and sample 4, an industrial analog of calcium grease Uniol-2.

Due to the chelating groups –OH, $-NH_2$, –CONH, –COOH, $-PO(OH)_2$, hydrophobic chelate complexes are formed, which give homogeneity, colloidal stability, and provide effective greasing properties to thixotropic systems [7]. As shown in Table, the obtained thixotropic systems of samples (1, 2, and 3) are characterized by improved tribological characteristics as well as increased oxidation resistance and colloidal stability. Sample 1 of the grease composition exhibits slightly worse indicators (Table) of oxidation resistance and colloidal stability, which is explained by the lower concentration of biosurfactants, vaterite modification of calcium carbonate crystallites, and vaterite, which are less stable [1,6,7].

Mechanical stability is the ability of thixotropic systems to maintain their consistency during operation. Samples 1, 2 and 3 of thixotropic systems were made according to the consistency of NLGI (National Lubricating Grease Institute) class 2, which is determined by the penetration index with stirring for 60 double strokes at 25^{0}C. The second NLGI class is the most common among industrially produced greases, and their «working» penetration value is in the range



a b c

Fig. 1. XRD patterns of nanodispersed calcium carbonate: (a) sample 1; (b) sample 2; and (c) sample 3

from 265 m·10^{-4} to 295 m·10^{-4}. For samples 1, 2 and 3 of grease compositions, this indicator meets these boundary conditions.

One of the most important indicators of the thermal stability of greases is the dripping point and the maximum operating temperature. According to Table, the dripping point of the samples 1, 2 and 3, at which the grease changes from a plastic solid to a liquid state, is more than 250⁰C.

Figure 4 shows the results of differential thermal and thermogravimetric analyses of the sample 3 grease composition. Starting from a temperature of 327⁰C, a series of low exothermic peaks are observed on curve 1 (Fig. 4) at 327⁰C, 395⁰C, 401⁰C and 511⁰C, which characterize the thermal oxidative destruction of the dispersion medium and the dispersed phase of the grease sample. Curve 2 (Fig. 4) demonstrates that the grease sample 3 remains thermally stable up to 251⁰C, which indicates the high resistance of the grease composition to thermal transformations. When the temperature rises to 323⁰C, a sharp weight loss of the grease is observed due to intensive chemical decomposition and evaporation of its dispersed phase.

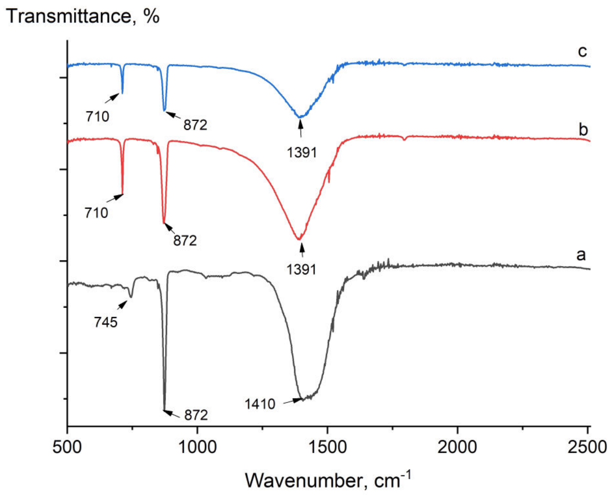


Fig. 2. Representative IR spectra of nanodispersed calcium carbonate: (a) sample 1; (b) sample 2; and (c) sample 3

According to derivatographic studies and calculated by the dripping point, the upper temperature limit for the use of the developed grease (sample 3) is 160–170⁰C. Similar data apply to samples 1 and 2. It is known that calcium greases in oil dispersion media are operable at temperatures more than 150⁰C and exhibit effective greasing properties [11].

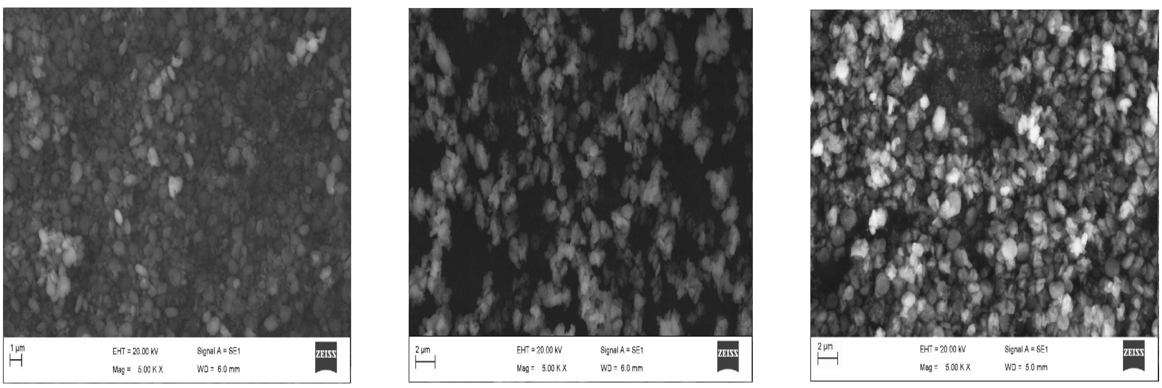
Thus, nanodispersed calcium carbonate of thixotropic systems was prepared by the carbonation method as a thickener or emulsifier-stabilizer for the development of calcium grease compositions with improved performance characteristics and not inferior to the calcium grease of the industrial analog Uniol-2.

Conclusions

1. The nanodispersion carbonate core of thixotropic systems was prepared by carbonation, the interaction of carbon dioxide with calcium hydroxide in a microemulsion system in which the internal dispersed phase, a mixture of water and methanol with calcium hydroxide, is bound to the oil-toluene dispersion medium (petroleum or synthetic oils) into a single system by a synthesized biosynthetic surfactant and the formation of a grease thickener as an emulsifier-stabilizer.

2. The formation of calcium carbonate crystallites of thixotropic systems of ellipsoidal and spherical shapes, vaterite, and calcite polymorphic modification with size from 6–15 nm to 34–51 nm was confirmed by X-ray diffraction analysis and scanning electron microscopy.

3. The developed calcium grease compositions based on the synthesized emulsifier-stabilizer show improved protective and tribological properties, as well as increased oxidation, and colloidal stability.



a b c

Fig. 3. SEM images of nanodispersed calcium carbonate: (a) sample 1; (b) sample 2; and (c) sample 3

Properties of samples of calcium grease compositions

Sample No.	Samples of grease composition	Properties of samples of grease composition					
		Dropping point ^{0}C	Tribological characteristics on four ball machine at the temperature of (20±5)^{0}C		Penetration after 60 strokes at 25^{0}C, m·10^{-4}	Colloidal stability, % of extracted oil	Resistance to oxidation: increase in acid number (150^{0}C, 10 hours), mg KOH/g
			critical load (Pc), N	welding loading (Pw), N			
1	Sample 1	>250	1381	5841	286	3.1	0.05
2	Sample 2	>250	1568	6174	279	2.6	0
3	Sample 3	>250	1568	6546	275	2.5	0
4	Sample 4	>230	1039	3222	330	7.5	1.65

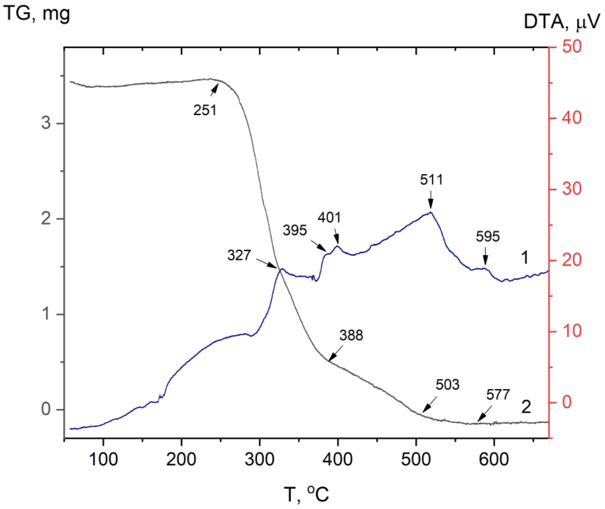


Fig. 4. DTA (1) and TG (2) curves of grease composition (sample 3)

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ОДЕРЖАННЯ НАНОДИСПЕРСНОГО КАРБОНАТУ КАЛЬЦІЮ ДЛЯ ТИКСОТРОПНИХ СИСТЕМ МЕТОДОМ КАРБОНАТАЦІЇ

Л.Ю. Бодачівська

Запропонована міцелярна модель одержання нанодисперсного карбонатного ядра тиксотропних систем, за якою процес карбонатації перебігає у інвертній мікроемульсії – системі, в якій внутрішня дисперсна фаза, водно-метанольна суміш з гідроксидом кальцію, зв'язана з дисперсійним оливно-толуольним середовищем (нафтові чи синтетичні оливи) в єдину систему синтезованою біосинтетичною поверхнево-активною речовиною з подальшим барботуванням діоксидом вуглецю в системі гідроксид кальцію та утворенням загусника мастил, як емульгатора-стабілізатора. Утворені кристаліти карбонату кальцію тиксотропних систем еліпсоїдальної та сферичної форм, фатеритної та кальцитної поліморфної модифікації з розміром від 6–18 нм до 34–51 нм підтверджено рентгеноструктурним аналізом та скануючою електронною мікроскопією. Розроблені кальцій-вмісні мастильні композиції на основі синтезованого емульгатора-стабілізатора характеризуються покращеними захисними та трибологічними властивостями, підвищеною стабільністю до окиснення та колоїдною стабільністю. Мастила призначені для змащування вузлів тертя машин і механізмів.

Ключові слова: синтез, нанодисперсне карбонатне ядро, поверхнево-активна речовина, тиксотропні системи.

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Keywords: synthesis; nanodispersed carbonate core; surfactant; thixotropic systems; grease composition.

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