

Продемонстрована можливість застосування азотвмісних поверхнево-активних речовин рослинного походження в якості компонентів дисперсної фази уреатних тиксотропних пластичних систем. Виявлено, що сечовина – продукт взаємодії аміноамідів стеаринової кислоти з ізоціанатом – є ефективним загусником нафтових олів. Введення до складу уреатного мастила поліфункціонального пакету олеопридадок покращує його змащувальні, антиокислювальні та екологічні характеристики

Ключові слова: уреатне мастило, аміноамід, ізоціанат, пакет олеопридадок, трибологічні характеристики, біорозщеплюваність

Продемонстрирована возможность применения азотсодержащих поверхностно-активных веществ растительного происхождения в качестве компонентов дисперсной фазы уреатных тиксотропных пластичных систем. Виявлено, что мочеви́на – продукт взаимодействия аминиами́дов стеариновой кислоты с изоцианатом – является эффективным загустителем нефтяных масел. Введение в состав уреатной смазки полифункционального пакета олеопридадок улучшает ее смазывающие, антиокислительные и экологические характеристики

Ключевые слова: уреатная смазка, аминиами́д, изоцианат, пакет олеопридадок, трибологические характеристики, биоразлагаемость

DEVELOPMENT OF COMPOSITIONS OF UREA GREASES ON AMINOAMIDES OF FATTY ACIDS

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1. Introduction

As present, up to 30 % of all generated energy is used in the processes of friction. About 4.5 % of energy can be saved by optimizing the application of lubricants [1]. Properly chosen oils simplify the design of machines, reducing their metal consumption and wear of parts, allow their term of inter-lubricating operations to last considerably longer and as well as to cut costs of equipment maintenance.

New technologies put forward strict requirements to the developers of oils. Lubricants must withstand overheating, hold to the surfaces at significant speeds, should not flow out of the bearings, possess high water resistance, protect metal parts from corrosion, etc. Modern oils are increasingly employed for the entire lifecycle of a mechanism without replacement and refill.

Lubricating compositions with a wide temperature working range and the required level of tribological, rheological and environmental characteristics have been in high demand recently, those stable at high temperatures and efficient in the presence of moisture. The aforementioned criteria are matched to a certain extent by the polyurea or urea greases (UG) [2]. In this case, technological progress and more strict regulations of environmental protection require a continuous optimization of the formulation-technological parameters, as well as conditions for the synthesis of these products. Article [3] highlighted the prospects of introduction to the

composition of lubricant the products of oleochemistry. The composition of lubricating and cooling liquids and plastic greases is increasingly added with the components of dispersion medium based on the sunflower or rapeseed oil. Saponified fatty raw materials are employed as thickeners. There are developed and applied multifunctional oleoadditives that are able to improve anti scratch, anti wear, anti corrosive and anti-oxidation properties [4, 5].

Given the stated above, it is obvious how relevant is the research into the possibilities to extend the scope of application of nitrogen-containing surface-active substances (SAS), obtained from renewable raw materials.

2. Literature review and problem statement

The first aliphatic polyurea and the process of its obtaining from diisocyanates and diamines was patented in the 40s of the 20th century by the global company DuPont (USA). Another American company Standard of Indiana patented polyurea in 1955 as a thickener for oils. Creation of the new type of lubricant material was predetermined by the lack in those days of chemically- and thermally resistant thickeners for silicone oils. UG proved to be non-corrosive, high-melting, chemically- and thermally resistant. On the other hand, UG is not much more expensive than the appropriate oils obtained on the same dispersion media. This

explains sufficiently high share of UG in the overall balance of using the plastic greases in the industrially developed countries of the world (in 2015 – 6.35 %). In this case, in North America – 7.19 %, Europe – 5.12 %, China – 4.9 %, and in Japan – even 27.91 % [6]. Constantly growing volume of the UG production is observed against the background of declining total world tonnage of plastic oils.

Of all the classes of commercially available thickeners for high-temperature lubricants that are represented in the market, the UG thickeners offer the widest range of operational characteristics. For the synthesis of di-, tri-, tetra- and polyurea thickener (by the number of groups $-\text{NH}-\text{CO}-\text{NH}-$ in a molecule), researchers use various combinations of amines and isocyanates [7]. Papers [8, 9] presented different mechanisms of their synthesis. Articles [10, 11] describe the properties of resulting lubricating compositions.

Based on di- or tetraurea, the greases are received that are suitable for the operation under extreme conditions at high temperatures and loads [12]. UG do not lose their properties in contact with water, petroleum products, aggressive and cleaning substances. In other words, where in most cases traditional multi-purpose oils remain ineffective or not applicable at all [13].

Increasingly, the UG compositions include oils. Thus, article [14] describes the compositions of UG on diurea, obtained by the reaction of diisocyanate with the amines of different nature. Soybean or rapeseed oils are used as a dispersion medium. The grease is designed for electrical appliances and significantly reduces the noise of operation. According to patent [15], oils are used in the grease composition in a different context. Grease for the hinges of identical angular velocities of cars is a combination of petroleum oil, diurea, additives and fillers. Its formulation is complemented with castor, soybean, rapeseed, coconut oils, or their mixture as additives for giving the system oiliness and shine. Oils also improve lubricating properties by adsorbing on the metal surfaces, preventing contact between them and reinforcing the effect of anti wear and anti scratch additives.

We could not find any evidence of using, for the synthesis of a UG thickener, the nitrogen-containing surface-active substances of the aminoamide type. There are no data on the introduction of oleo-additive packets into the composition of these greases either.

In Ukraine, the first samples of UG were developed in the 80s of the last century [16], but they have not been commonly employed. This is explained by the insufficient awareness of consumers of the possibilities of the given type of lubricants, certain conservatism of experts in the field of lubricants, as well as the lack of raw material components. Aliphatic amines with the content in the hydrocarbon chain of up to 20 carbon atoms and isocyanates of the type 2,4-toluene diisocyanate (TDI) or 4,4'-diphenylmethane diisocyanate (MDI) are not manufactured in Ukraine. However, these products are commercially available as they are imported to produce a wide range of chemical products. At the same time, Ukraine is a powerful producer of oils and animal fats – promising raw materials base for the synthesis of organic oleochemical substances of different purposes. The products of oleochemistry are able to replace those imported petrochemical ones. Scientists from the Institute of Bioorganic Chemistry and Petrochemistry of the Ukrainian NAS developed technologies of comprehensive utilization

and processing of oils for biosynthetical SAS, in particular, amino amides, imidazolines, higher fatty acids sulfanes, phosphorus-containing compounds, etc. [17, 18].

A generalized scheme of amidation reaction of individual fatty acids or triacylglycerides of animal fats or oils by diamines with obtaining amino amides can be represented in the following way (Fig. 1) [19, 20].

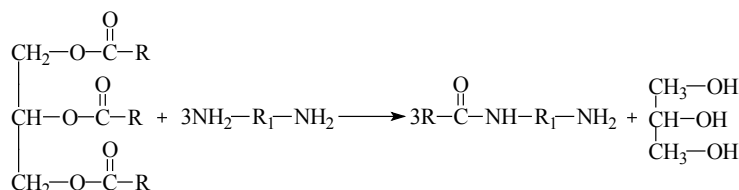


Fig. 1. Scheme of amidation reaction of fatty raw materials

Thus, the lack of commercially available lubricating materials such as UG produced in Ukraine, the uniqueness of properties of these products, availability of bio raw materials for the synthesis of components of thickeners and additives predetermine the prospects of work aimed at creating competitive urea lubricating compositions. Given the above, of interest is the research into the possibility of using the nitrogen-containing oleochemical surface-active substances (SAS), in particular amino amides of fatty acids, as components of a UG thickener.

3. The aim and tasks of research

The aim of present work is to develop, based on the biosynthetic SAS, the compositions of UG with improved ecological characteristics, to be operated in a wide range of temperatures, speeds and loads, resistant to mechanical destruction and the effect of oxidative factors.

To accomplish the set aim, the following tasks were solved:

- to synthesize amino amides of fatty acids and to analyze their chemical structure;
- to establish the possibility of obtaining a UG thickener by the interaction of amino amides with isocyanate and thixotropic plastic systems based on it;
- to explore technological parameters of UG manufacturing and its properties;
- to evaluate the effectiveness of introducing the oleo-additives to the composition of UG.

4. Materials and methods for examining the structure of amino amides, urea thickener and the properties of urea greases

In order to synthesize the high-molecular primary amine, we improved the method of fatty acid amidation with diamines. We employed stearic acid (HSt), ethyldiamine (EDA) and diethylentriamine (DETA). The synthesis was conducted in the medium of tetrahydrofuran (THF). As a catalyst, we used potassium tert-butoxide. In order to separate the target product from the dispersion, we first under vacuum distilled THF and then the formed sediment of the product and the catalyst was dispersed in ethyl acetate and washed with a solution of sodium chloride (NaCl). The isolated water dispersion of NaCl was cooled. The sediment

of salt was filtered out, then we distilled THF from the filtrate, which was used in the subsequent experiments. The organic phase was washed out over the freshly burned CaCl_2 , and then under vacuum we distilled THF. The product was dried to a constant mass and thus we received aminoamide of stearic acid (AA) with an almost quantitative yield. The progress of the reaction was controlled by a change in the concentration of amines by the potentiometric titration. It was found that the reduction in amine number indicates the progress of the basic reaction with the formation of amino amides.

Instead of toxic monomeric isocyanates, which require special safety measures, we used the so-called “grey” diphenylmethane diisocyanate (Crude MDI) or polyisocyanate (PIC), with a mass fraction of isocyanate groups of 35–38 %, to obtain a UG urea thickener. This is a viscous liquid of brown color with a characteristic odor.

All UG samples are made on the basic petroleum oil containing 72.0 % by weight of paraffin-naphthenic hydrocarbons, 21.6 % of light and 4.7 % of medium aromatics, as well as 1.7 % of resins, by a known technology [21]. We prepared individual solutions of PIC and AA in petroleum oil. It was heated to 70 °C and mixed in the reactor, equipped with a heater and a stirring device. Prepared individual solutions of PIC and AA in oil with oil, heated to 70 °C and mixed in the reactor, equipped with a heater and a mixing device. Reaction between isocyanate and amines is exothermic and proceeds at high speed. By-products that must be removed do not form. Next, the suspension that formed was heated to 150 °C and cured for 30 min. The samples were cooled to 20 °C and homogenized on the laboratory three-roll wearing machine DW-3 (Germany).

By applying the above method, we synthesized the samples of urea thickener by the interaction between PIC with AA at molar ratio of 1:2.5 in the medium of petroleum oil. Concentration of the disperse phase is 18 % by weight.

The structure of synthesized substances was analyzed using the infrared spectrometry. Spectra were recorded in a thin film on the IR- spectrometer with Fourier transform Thermo Nicolet Nexus FT-IR (USA). Thermal properties of UG were investigated in static atmosphere of air using the derivatograph Q-1500D (Hungary) with computer data registration. Registration parameters of the thermogram: batch is 106.8 mg; heated from 20 to 1000 °C, heating rate is 10 °C/min.

Indicators of dripping temperature and the colloidal stability of UG were determined in line with ASTM D 566 and GOST 7142. Mechanical stability of UG was assessed by a change in the penetration index after prolonged stirring ($P_2 - P_1 = \Delta P$). In accordance with ASTM D 217, oils are destroyed in a standard mixer from the penetrometer. P_1 is determined after 60, and P_2 – after 100 000 double moves. A change in the state of grease consistency during prolonged stirring characterizes a predisposition or resistance of grease to the thixotropic destruction.

Resistance of the samples of grease to the oxidation was analyzed by a change in acid number after treatment at 130 °C for 6 hours in accordance with GOST 5734. Tribological characteristics – critical loading critical (P_c) and welding load (P_w) – was estimated on the four-ball friction machine according to GOST 9490. Environmental characteristics were determined by GOST 4247:2003 “Petroleum products. Method for determining the biodegradation (CECL 33-A-93, NEQ)”.

5. Results of exploring the structure of amino amides and the operating characteristics of urea lubricant compositions

By their physical state, monoamino amides of stearic acid are the paraffin- or grease-like substances of brown color, well soluble in ethanol and isopropyl alcohols, partially in water, kerosene and p-xylene. They are not soluble in hexane and isooctane.

The IR spectra of synthesized AA are practically identical (Fig. 2). There are observed bands at 3295 cm^{-1} of valence fluctuations of NH group, at 2917 and 2849 cm^{-1} – valence fluctuations of CH bond in CH_3 -, CH_2 - and CH-groups. At 1635 cm^{-1} , there are observed bands of valence fluctuations of NCO groups, at 1549 cm^{-1} – deformational fluctuations of NH bond, at 1462 and 1399 cm^{-1} – deformational fluctuations of CH bond in CH_2 - and CH-groups, at 1119 cm^{-1} – valence fluctuations of SN bond. At 719 cm^{-1} , there are visible bands of beyond-the-surface deformational fluctuations of CH bond of the hetero chain [22].

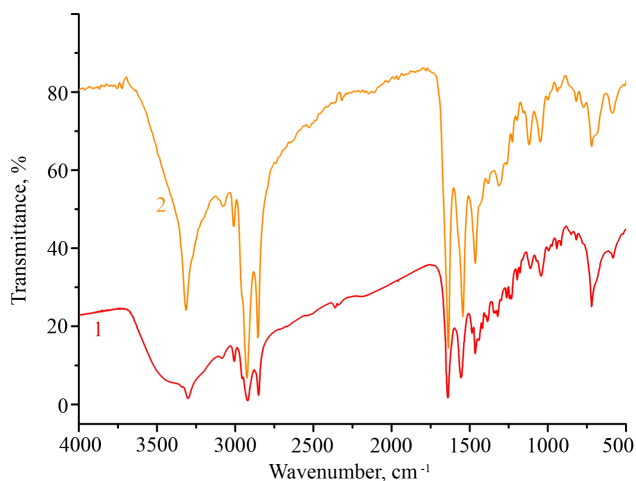


Fig. 2. Infrared spectra of stearic acid amino amides based on: 1 – ethylenediamine; 2 – diethylenetriamine

Fig. 3 shows the IR spectra of UG and its individual components. The thickener was synthesized on EDA. Isocyanate groups of $-\text{N}=\text{C}=\text{O}$ PIC match the asymmetric valence fluctuations in the region of 2280–2230 cm^{-1} . This band is absent on the spectrum of UG, testifying to the interaction between isocyanate and AA and the formation of a urea thickener.

In order to determine the upper temperature limit for the application of UG, we adapted the method of derivatographic analysis, which is based on simultaneous measurement of mass and enthalpy of the material while it is heated. Derivatography is a combination of the two most common thermographic methods: differential thermal analysis (DTA) and thermographic analysis (TGA), and it allows determining the temperatures at which the physical and chemical transformations occur in a thickener. In the course of derivatographic analysis of the sample of a grease, the curves are simultaneously recorded (Fig. 4): DTA, thermogravimetry (TG) and differential thermogravimetry (DTG).

Table 1 gives the results of examining the influence of the AA structure on the properties of thixotropic systems. Both synthesized greases are characterized by high dripping temperature, colloidal and mechanical stability, but insufficient lubricating properties.

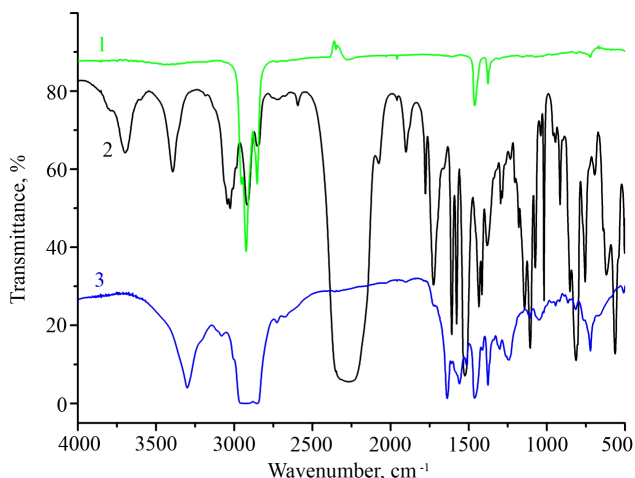


Fig. 3. The infrared spectrum of urea grease and its components: 1 – petroleum oil; 2 – polyisocyanate; 3 – grease

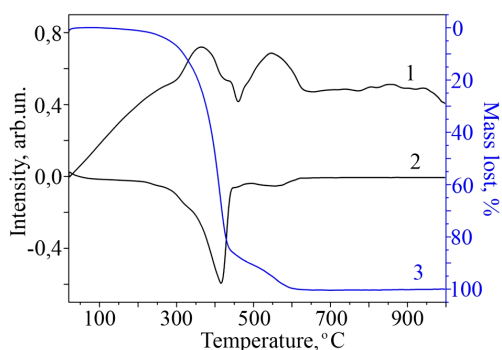


Fig. 4. Derivatogram of urea grease on the thickener with ethylenediamine: 1 – curve of differential thermal analysis; 2 – differential thermogravimetry DTG; 3 – thermogravimetry

The presence of polyurea as a thickener is not an absolute guarantee of high efficiency of greases. The unique properties of UG are demonstrated only by the balanced compositions of optimum formulation with correctly chosen basic oils, additives, and fillers. In order to create a grease composition with improved lubricating and anti-oxidation characteristics, the composition of grease on EDA is introduced with a packet of SAS additives that include:

- “Additive Eterol-S” (Ukraine) – sulphur-containing ethyl ester of higher fatty acids of rapeseed oil with a mass fraction of sulphur 10 % by weight.
- “Additive to petroleum products Fosfoldin” (Ukraine) – a product of condensation of phosphatide concentrate with N,N'-bis(2-hydroxyethyl)-ethylenediamine;

Table 1 gives the results of comparative studies of the properties of the new UG and commercially available oil Politerm-Multipurpose (Russia), which is designed for use in friction units of technological equipment in the temperature range from –20 to +150 °C. The oil Politerm-Multipurpose is made on petroleum oil and polyurea thickener with the addition of packet of additives consisting of an anti wear additive and an oxidation inhibitor.

6. Discussion of results of exploring the possibility of using the biosynthetic surface-active substances in the composition of urea greases

The PIC, used for the synthesis of a urea thickener, is a mixture of MDI (mainly 2,4'- and 4,4'-isomers), triisocyanates and polyisocyanates. Fig. 5 shows a general scheme of interaction between PIC and amino amides.

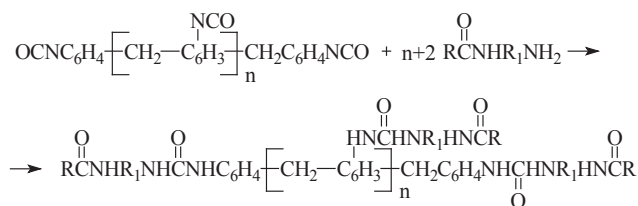


Fig. 5. Scheme of reaction between polyisocyanate and amino amides

Table 1

Properties of the developed urea greases on the amino amides of different structure and commercially available oil Politerm-Multipurpose (Russia)

Indicator	GOST, ASTM	Grease							
		EDA	DETA	EDA with additives	Poli-term				
Colloidal stability, %	7142	4.0	7.2	4.5	8.0				
Dripping temperature, °C	D 566	256	233	257	226				
Acid number gain, mg KOH/g	5734	0.49	0.4	0.25	0.37				
Penetration, mm·10 ⁻¹	D 217	270	312	272	278				
– P ₁						302	360	310	346
– P ₂						32	48	38	68
– ΔP									
Tribological properties, H	9490	657	735	980	921				
– Pc						1568	1568	2450	2323
– Pw									
Biodegradation, %	CECL33-A-93	–	–	36.7	27.6				

The ratio of reagents applied for the synthesis of a thickener leads to the full consumption in the course of reaction between PIC and AA and allows receiving the urea with maximum yield. When compared with the classical diurea, when employing the PIC, the number of urea groups increases in a thickener’s molecule. According to authors in [23], it has a positive effect on the lubricating and operating characteristics of the system as a whole.

All plastic greases are sensitive to high temperature, which leads to the melting of thickener and thermal oxidative destruction of molecules in a dispersion medium. It is obvious that high temperature greases must be characterized by a high level of thermal resistance. In terms of the stability of a dispersed phase, the indicators of thermal resistance are the dripping temperature and a maximal working temperature [24]. Dripping temperature is the temperature at which grease passes from a plastic solid state into a liquid state. By using this indicator, it is possible to characterize the nature of a thickener on whose base the grease is made. Dripping temperature of high-temperature oils must exceed 230 °C.

On the curves of TG grease on EDA (Fig. 4) the initial horizontal section to 200 °C indicates high resistance of UG to thermal transformations. At reaching 300 °C, there is a vertical ledge on the curve, which indicates intensive chemical degradation and intensive evaporation of dispersed medium of the lubricant. On the DTA curves there are two exothermal effects in the temperature range of 350–550 °C, which characterize intensive thermal oxidative destruction of the dispersion medium and the urea thickener. Results obtained by this method allow us to define the upper temperature limit of the UG application, made on the basic petroleum oil. This indicator is in the range of 150–200 °C. At a change in the dispersion medium, the upper temperature limit may shift towards one or another side.

The character of the TG curve in Fig. 4 testifies to a 100 % loss of weight by the grease when heated to 600 °C. UG does not form ashes in contrast to soap lubricants. This provides the given type of greases with an advantage when used at high temperatures. Soot and deposits of sludge are eliminated on the friction surfaces, which contributes to prolonged lifecycle. On the surfaces of friction eliminated fouling and deposits of sludge, which leads to the growth of the life of the equipment.

AA differ by the structure of amine component. DETA contains one group more $-\text{NH}-\text{CH}_2-\text{CH}_2-$ and, due to it, has the capability to create additional hydrogen bonds when forming supermolecular structures of the dispersed phase of a thixotropic colloidal systems. At first glance, this circumstance should positively influence the properties of UG in general. However, as evidenced by the Table, the rheological characteristics of oil on DETA deteriorate in comparison with EDA. The grease is diluted; its dripping temperature reduces, as well as colloidal stability. On the IR spectra of ED and DETA (Fig. 2) there are no absorption bands of C=N bond at 1605 cm^{-1} , characteristic for imidazolines. That is, these products are absent in the system of a thickener and only the linear AA are formed by the amidation reaction. Probably, the synthesis of urea thickener and the strength of its structural frame in the grease on DETA are negatively affected by the molecule ramification and steric factors. Reactivity of AA deteriorates. The probability of the formation of intermolecular hydrogen bonds becomes lower.

Table 1 gives data on the mechanical stability of the synthesized UG. It should be noted that this is one of the most important parameters to evaluate the operating characteristics of anti-friction lubricants. A lubricant resistant to mechanical destruction does not change the structure, is not diluted and does not flow out of a friction unit. Operation lifecycle of equipment is extended. The difference $P_2 - P_1 = \Delta P$ evaluates mechanical stability of lubricants as follows: at $\Delta P < 30$ – excellent; at $\Delta P = 30 - 60$ – good; at $\Delta P = 61 - 100$ – satisfactory; at $\Delta P > 100$ – unsatisfactory [25]. It may be stated that although the mechanical stability of both UG is quite high, the grease on EDA has significant advantages by this indicator.

The presence of a larger amount of nitrogen and amine groups in the molecules of a thickener exerts a positive influence on the tribological and anti-oxidation properties of lubricants on DETA. Moreover, the product of interaction between PIC and AA is the inhibitor of group 1 that terminates

the chains of oxidation by the reaction with peroxide radicals, forming a polar transient complex $\text{ROO} \cdot \bullet \bullet \bullet \text{H} \bullet \bullet \bullet \text{In}$. These inhibitors usually include phenols, naphthols, secondary amines, aminophenols, etc. [26].

According to data in Table 1, the introduction into a UG composition of the packet of oleo-additives improves thermal, anti-oxidation, volumetric-mechanical and environmental characteristics. Due to the inhibiting action of the thickener and the additive Fosfolidin, resistance of the grease to the action of oxygen increases. UG, at gain in acid number, at high temperatures, demonstrates better anti-oxidation properties compared to the grease Politerm-Multipurpose. In addition, the application of Fosfolidin additive helped to improve the antiwear properties of UG. Introduction to the composition of UG of sulfanes of plant origin increased the level of anti scratch characteristics. We observed a growth in Pw by almost 1000 H with neither corrosion nor unpleasant odor. High mechanical stability of UG allows predicting their long-term operation in friction units without softening and leakage. The new lubricant is better than the grease Politerm-Multipurpose by environmental characteristics as well. The index of biodegradation is reduced by almost 15 % in comparison with the analogous product.

By summarizing results that we received in comparative studies, we can state that UG with the additives of plant origin could be used as a high-temperature anti friction lubricant under conditions of high loads and in a wide temperature range.

7. Conclusions

1. By applying the stearic acid amidation with ethylenediamine and diethylentriamine, we synthesized monoamino amides of linear structure. The composition and chemical structure of the compounds were defined by a complex of spectrometric methods of analysis. We proved the absence of imidazolines in the composition of reaction products.

2. We demonstrated the possibility of applying the amino amides of plant origin for the synthesis of a urea thickener. The urea greases obtained are characterized by a high level of mechanical and colloidal stability. Their upper temperature limit of application, established by the method of derivatographic analysis, amounts to 150–200 °C. It was found that depending on the structure of diamines, it is possible to receive a thixotropic colloidal system with required properties.

3. It was established that the introduction to the composition of an urea grease of a polyfunctional packet of oleo-additives improves the lubricating characteristics by 4 degrees of loading row according to GOST 9490 Pc grows and Pw – by 8.

4. It was discovered that the joint action of a urea thickener and oleo-additives improves the level of anti-oxidative resistance of grease at high temperatures. We observed a decrease in the indicator of acid number gain by almost two times.

5. It is proved that applying the biosynthetical SAS in the formulation of greases improves the biodegradation of a lubricating composition by 15 %, which is an important factor in protecting the environment.

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