МАТЕРИАЛОВЕДЕНИЕ В МАШИНОСТРОЕНИИ

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DEVELOPMENT OF THE METHOD AND OPTIMIZATION OF THE COMPOSITION AND MODES OF OBTAINING THE BIODEGRADABLE GREASE WITH THE LITHIUM-CALCIUM THICKENER

It is noted that the development of biodegradable lubricants is an integral part of the development of a modern "green" economy. The distinctive features of the proposed method are described for producing a biodegradable grease on a mixed lithium-calcium thickener, providing for the introduction of alkaline initial components of the dispersed phase (lithium hydroxide monohydrate and calcium hydroxide) into the reaction mass not in the form of their aqueous solutions, but in a powdery state, and the exception of prolonged exposure to water and high temperature on a component of a dispersion medium of plant origin (rapeseed oil) in the process of lubricant synthesis. Along with this, it was proposed to use a highly refined oil of group III according to the API (American Petroleum Institute) standard as a mineral component of the dispersion medium. This provides, in aggregate, the higher stability of the rheological and tribological characteristics of the grease (for at least 12 months) at a given level of biodegradability. The experimental-statistical mathematical model of the process of obtaining the biodegradable lithium-calcium grease is developed, which makes it possible to determine the parameters of the component composition (the content of the mixed lithium-calcium thickener in the grease and the content of lithium stearate in the mixed thickener) and the synthesis modes (the heat treatment temperature of the reaction mass) to achieve the given level of the main characteristics of the finished grease (penetration, dropping point) while ensuring its biodegradability of at least 80 %.

Keywords: *grease, dispersion medium, mixture of vegetable and mineral oils, dispersed phase, lithium-calcium thickener, rheological and tribological properties, biodegradability*

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Introduction. Creation and use of so-called "green" lubricants are currently receiving increasing attention, for at least two reasons. One of them is due to the need to protect the environment, since lubricants currently manufactured mostly on the basis of mineral oils, getting into the environment at the stages

of manufacture, transportation, storage, use and disposal, create biotoxicological threats to humans and all living organisms. The second reason seems to be related to the search for sources of cheap renewable raw materials for lubricants as an alternative to gradually depleted oil reserves.

One of the promising solutions to both of these problems is the use of raw materials of plant origin [1–7]. It is known that vegetable oils consist mainly of triglycerides of fatty acids. Their chemical properties are mainly due to the unsaturated fatty acids contained in them, since the latter are the most reactive (first of all, this applies to their polyunsaturated representatives), and their total content in oil is usually high. The structural features of triglycerides of fatty acids, of course, have a significant impact on the tribological properties of vegetable oils. Thus, the presence of polyunsaturated acids in the composition of vegetable oils with two- and three-fold double bonds in their molecular structure gives them the functions of natural surfactants, which favorably affects the formation of boundary layers with low shear resistance and increases the wear resistance of solids [8–11]. However, it is necessary to keep in mind such significant disadvantages of vegetable oils as their easy oxidation susceptibility in air and their tendency to polymerization over time, due, in particular, to the presence of unsaturated bonds in the structure of the triglyceride molecule. Therefore, the use of lubricants containing a dispersion medium completely in the form of vegetable oil (or a mixture of vegetable oils) is advisable only in cases of a relatively short period of their use (flow lubrication, frequent replacement of the lubricant), provided that they are stored in sealed containers without air access.

In this regard, it seems more rational to create greases based on a mixture of vegetable and mineral oils with a choice of the ratio between their content, based on the required level of tribological properties and the desired transience of the grease biodegradation process. This will ensure the preservation of the structural state and consumer properties of the lubricant for a certain period of time, taking into account the specifics of the lubrication of the friction unit and the duration of storage and use of the grease.

Of all types of lubricants (liquid, plastic, solid, gaseous), plastic ones are produced in the widest range, firstly, due to their unique property — thixotropic character (the ability to exhibit the properties of either a solid or a liquid body, depending on the loading conditions), and secondly, due to the possibility of varying their rheological and tribological properties within a relatively wide range, using a large number of dispersion media (DM), dispersed phases (DP) and additives of different structure and nature [12–14]. At the same time, of course, each of the DM and DP variants has its own advantages and disadvantages, so quite often to obtain the required set of properties of a grease, they resort to using a dispersion medium in the form of a mixture of oils in various combinations, and the dispersed phase in its composition can be either single (consisting of one substance) or heterogeneous (consisting of several components of the same or different physical and chemical nature) [15]. The use of heterogeneous DM makes it possible to combine the technical and economic advantages of each of the options separately, thereby expanding the functionality and application areas of the grease on a mixed thickener, as well as reducing its cost. In particular, the use of a mixed lithium-calcium thickener makes it possible to combine increased water resistance, high load-bearing capacity of the lubricating layer and a lower cost of the calcium component with high temperature resistance and improved lubricating properties of the lithium component.

The quality level of a biodegradable grease is determined by a wide range of its rheological (penetration, dropping point, colloidal and mechanical stability, etc.) and tribological (ultimate load, welding load, load wear index, wear index, etc.) properties, which, in turn, depend on its component composition and a number of parameters of the technological process of synthesis of biodegradable greases. At the same time, the level of properties of a grease is largely determined by the structure of its dispersed phase (the shape and size of the fibers, the degree of branching, the amount of DP in the lubricant). The biodegradability of a lubricant is determined by the amount of biodegradable components contained in it, in particular, of vegetable or animal origin.

The objective of this work is to develop a method and optimize the composition and modes of obtaining a biodegradable grease having a dispersion medium in the form of a mixture of oils of vegetable and mineral origin and a mixed lithium-calcium thickener.

Research method. To obtain experimental samples of plastic lubricants, we used mineral oil of group I according to the API standard of the И-40А (I-40A) brand [16] and high-purity oil of group III according to the API standard of the НС-4 (NS-4) brand (TU BY 300042199.037-2015) produced by OJSC Naftan, rapeseed oil [17] produced by JSC "Raps", 12-hydroxystearic acid (TU 38 101 721), calcium hydroxide [18], monohydrate lithium hydroxide [19], depressant additive K-110 (TU 0257-037-40065452-03), adhesive additive Petrolad 484 BD (manufactured by BRB company), multifunctional additive ДФ-11 (DF-11) (TU 0257-005-00044434-99).

The quality of the grease was evaluated by the penetration index [20], dropping point [21], colloidal stability [22], mass fraction of mechanical impurities [23], water content [24] and tribological characteristics determined on a four ball machine according to [25]. The methods used in this paper for assessing the biodegradability of greases are based on studying the dynamics of fatty acid transformations and determining the degree of their destruction within 28 days, similar to the approach described in [26]. In this case, the fatty acids were converted to their methyl esters, and

the biodegradability was determined based on the content of fatty acids in the samples of methyl esters, established by gas-liquid chromatography (GLC analysis) using an Agilent 7820A GC gas chromatograph (Agilent Technologies, USA).

In order to take into account the time factor during storage, the rheological characteristics of the experimental biodegradable grease samples were tested on the day after their manufacture, as well as after 6 and 12 months of storage. In order to tighten the environmental impact during the storage period between the test stages, the biodegradable grease samples were placed in an open container under the influence of direct sunlight.

Analysis of methods for producing biodegradable greases on mixed thickeners. In recent years, a large number of biodegradable greases have been developed using vegetable oils (or their mixtures with mineral oils) on mixed thickeners, including lithium-calcium salts. In particular, a lubricant composition is known based on a mixture of mineral and vegetable (rapeseed) oils, thickened with lithium 12-hydroxystearate, and additionally containing polytetrafluoroethylene, polysiloxane liquid, a suspension of stearate and copper acetate in castor oil, as well as graphite modified with caprolactam oligomers [27]. The disadvantages of this biodegradable grease and the method of its preparation include the fact that during the manufacturing process, the vegetable oil comes into contact with water. As a result, the vegetable fats contained in the vegetable oil are hydrated to form fatty acids, which in turn react with the excess alkali required for the finished lubricant. As a result, the lubricant hardens during storage and becomes acidic, which leads to an increase in its corrosion activity when used in the friction unit.

In the work [28], an environmentally friendly lubricant is proposed containing as a base oil a mixture of mineral and vegetable oils thickened with lithium-calcium salt of 12-hydroxystearic acid, while sodium tetraborate, salphonated oil and glycerin are proposed as additives that improve tribotechnical properties. The negative aspects of this development include the low colloidal and mechanical stability of the greases, due to the heterogeneity of the structural framework of the thickener and its insufficiently uniform distribution in the volume of the finished lubricant. This feature is due to the fact that initially the thickener is formed in a limited reaction volume between the initial DP components (12-hydroxystearic acid and an aqueous suspension of a mixture of alkalis) without the participation of an oil dispersion medium. This complicates the structure formation of the spatial framework of the thickener, which is formed as an excessively thickened mass, which further causes its difficult dispersion in the dispersion medium, non-uniform distribution over the volume of the grease, and, as a result, a decrease in the rheological and tribological parameters and functional characteristics of the product. It should also be noted that the participation of vegetable oils in the technological process of preparing greases at long stages of thermomechanical processing of DP (thickener) to temperatures of 190–200 °C leads to difficult to predict thermochemical destruction of plant raw materials and the formation of harmful side components in the system. This, in turn, causes additional undesirable reactions and instability of the properties of the finished lubricant during storage.

Development of a method for producing a calcium-lithium biodegradable grease. Obtaining a biodegradable plastic lubricant using raw materials of plant origin, which would be characterized by high colloidal and mechanical stability, permissible tensile strength and minimal corrosion effect on friction units, stable properties during storage, while minimizing the influence of the composition of plant raw materials on the technological process, was part of the tasks of this work. The solution to this issue was found both in the selection of a rational combination of the components of the dispersion medium and the dispersed phase, and in the search for the optimal structure of the technological process and the level of its temperature and time parameters [29].

The first of these issues was solved by using a highly refined mineral oil corresponding to the API classification group III as one of the components of the dispersion medium, and synthesizing a binary dispersed phase in the form of a mixture of lithium and calcium salts of 12-hydroxytearic acid.

Hydrogenation and hydrocracking in the production of group III base oils have a significant effect on the chemical structures of the substance molecules included in mineral oils. In this case, both the stabilization of individual molecules due to the removal of heteroatoms (sulfur, oxygen, nitrogen) and the transformation of aromatic compounds into saturated naphthenic or paraffinic hydrocarbons due to their deep hydrogenation occur. In addition to hydrogenation, hydrocracking breaks down or cracks large molecules into smaller ones. In this case, large molecules with a more ordered and homogeneous structure can be formed again from small fragments. Thus, the main result of hydrocracking is the isomerization of paraffins. In this case, along with the saturation of aromatic compounds, the naphthenic rings are opened. All these processes lead to the almost complete removal of carcinogenic and pathogenic substances from the base oil, which can inhibit the growth of the number of microbes that multiply in the process of biodegradation [14].

Base oils of group III are white oils, odorless, with a low content of aromatic substances or do not contain them at all. The paper [30] provides data on the comparison of individual properties of various base oils, from which it follows that the API group III base oils have the same average quality value with vegetable oils or even slightly exceed some technical vegetable oils. This fact makes the use of API group III base oils in biodegradable lubricants promising.

The main objective criterion by which the material is classified as biologically safe lubricants is the degree

of biodegradability of at least 60 % [31]. However, group III base oils have a slightly lower rate of biodegradation relative to vegetable oils, which prevents them from completely replacing vegetable oils in the production of biodegradable greases, and it is necessary to establish an optimal ratio in the dispersion medium of the biodegradable plastic lubricant of vegetable oil and group III oil according to the API classification.

In a mixed calcium-lithium thickener, each of the salts of high-molecular-weight 12-hydroxystearic acid performs its function: the calcium salt causes a higher bearing capacity of the lubricating layer, and the lithium salt contributes to an increase in the dropping point, as a result of which the greases on a mixed calcium-lithium thickener will be characterized by increased load parameters at increased temperatures without the use of special additives and fillers.

The solution of the second part of the issue concerning the search for a rational structure of the technological process for obtaining greases based on vegetable oil should be considered taking into account the chemical composition of vegetable oils and the influence of contact with water and thermal effects on them. It is known that greases should have a slightly alkaline reaction. The mass fraction of free alkali in terms of NaOH, as a rule, is 0.1–0.2 %, and the mass fraction of free organic acids — no more than 1.5 mg KOH per 1 g of lubricant. This is necessary to give the grease anti-corrosion properties and increase storage resistance, since during storage, some oxidation of the base oils occurs with the formation of acidic products.

When using vegetable oils as a dispersion medium, this indicator becomes the most relevant, which is because of the diversity of the composition of vegetable oils, due to the content of various isomers of fatty acids, cyclic acids, and oxy-acids (both saturated and unsaturated). During storage, fats in vegetable oils often undergo profound changes, especially in the presence of water, due to their complex chemical composition and a significant number of unsaturated compounds. Vegetable oils consist mainly of esters of unsaturated fatty acids with one (oleic), two (linoleic) or three (linolenic) double bonds. Therefore, they are very unstable in contact with water, easily oxidized and get rancid. The cleavage (hydrolysis) of the ether bonds occurs with the accumulation of free fatty acids, which is expressed by an increase in the acid number. Under the influence of high temperatures, the processes of oxidation of vegetable oils are sharply accelerated, which proceed through the addition of oxygen molecules in unsaturated substances of vegetable oils through the double bond method with the formation of cyclic peroxide and an increase in the acid number of the oil. Due to this feature, it was necessary to minimize the impact of water and temperature on vegetable oils, which is especially important in the production of lubricants.

In general, to solve the given task, a variant of the construction of the technological process was proposed, which excludes the long-term effect of high temperatures and heat on vegetable oils. In this method, a technical solution is applied that makes it possible to almost completely eliminate the participation of water in the technological process of obtaining plastic lubricant. As a rule, in the production of greases, alkalis are introduced in the form of aqueous solutions. This is done in order to detach a water molecule from the composition of lithium hydroxide monohydrate or to convert calcium hydroxide into an active reactive state. Also, the use of aqueous solutions makes it possible to improve the uniformity of the introduction of alkalis into the reaction volume, since as they are introduced, the reaction mass significantly thickens, and, consequently, the dispersion processes deteriorate greatly, the contact of the reaction components becomes more difficult, and the rate of the neutralization reaction slows down. In the developed method, lithium hydroxide monohydrate and calcium hydroxide are introduced into group III base oil not in the form of aqueous solutions, but in a powdered state after the introduction and melting of 12-hydroxystearic acid in it. After that, the reaction mass is heated to a temperature of 110–115 °C with constant dispersion of the powdery components in the hydrodynamic dispersant to a nanoscale level and intensive mixing in the reactor in order to activate the neutralization reaction. Such effect helps to detach the water molecule in the lithium hydroxide monohydrate and remove the sorbed water of calcium hydroxide. The alkalis pass into the active state, which contributes to an increase in their reactivity. At the same time, they are distributed as evenly as possible over the volume of the reaction mass, ensuring the stability of the neutralization reaction throughout the entire volume of the reaction medium. Heating to lower temperatures does not guarantee the removal of water, and the use of higher temperatures is energetically impractical. Along with that, it should be noted that neutralization proceeds with the release of reaction water and a temperature level above 110–115 °C will cause its extremely rapid boiling, which can lead to a significant expansion of the reaction mass and its release from the reactor.

In this case, the chemical reactions accompanying the formation of the dispersed phase take place in the medium of group III oil, in which the thermomechanical treatment of the residual mass takes place with the achievement of a complete melt at a temperature of 190–200 °C (this oil is highly resistant to oxidation at elevated temperatures), and the vegetable oil is added only at the cooling stage. The proposed option eliminates the long-term use of vegetable oils in high-temperature technological operations and reduces the risk of degradation of their properties at the stage of obtaining a grease.

The studies carried out during the development of the component composition showed that when using in a grease more than 35 wt.% of group III base oils, it reduces its degree of biodegradation to less than 80 %,

which is unacceptable for biodegradable lubricants. The use of group III base oils in the composition of the grease in an amount of less than 30 wt.% worsens the dispersibility of the thickener in the volume of the dispersion medium of the grease, which, in turn, worsens its indicators such as colloidal stability and penetration. And when using 25 wt.% of group III base oils during the manufacture of the lubricant, its colloidal stability deteriorates to 16.5 %, and the penetration index exceeds $310 \cdot 10^{-1}$ mm (the lubricant passes to another penetration class — NLGI grade 1), while greases for ball/roller bearings, sliding friction units operating under moderate load and speed conditions should have a penetration index in the range of $(265–295) \cdot 10^{-1}$ mm (NLGI grade 2).

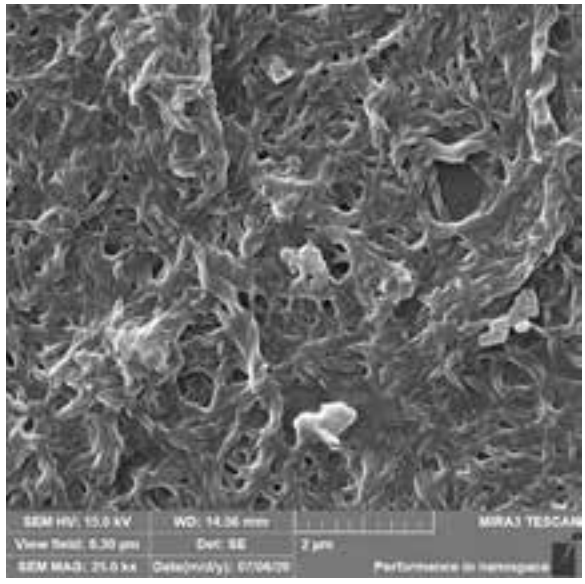
The study of images of the nanostructured dispersed phase of plastic lubricant samples obtained by scanning electron microscopy according to the method [32] showed that at the microlevel, the structure of the dispersed phase of the plastic lubricant obtained according to the proposed version of the composition of the dispersion medium and the technology [29] is characterized by a more uniform distribution of thickener fibers over the volume of the material than that of the plastic lubricant obtained according to the technological scheme described in [28], using a group I oil of И-40А (I-40A) grade according to API standard as a mineral component of the dispersion medium (Figure 1).

The DP fibers of the lubricant obtained according to the technology variant [29] have a large length (about 3–5 μm), and their diameter is 0.15–0.2 μm. They have a more pronounced spiral morphology, which should also contribute to the increased mechanical and colloidal stability of the plastic lubricant. At the same time, in the structure of the lubricant obtained according to the technological scheme [28], the remains of unreacted poorly dispersed initial components of the dispersed phase are visible, which indicates the incompleteness of the DP formation process in this case.

To determine the ability to preserve the properties of the obtained greases during storage, their parameters were determined according to standardized methods on the next day after manufacture and after 6 and 12 months of storage. During this period, the greases were stored in an open container at a temperature of 20–25 °C, accessible to sunlight.

The test results are presented in Table 1.

As a result of the tests carried out, it was found that the lubricant of the selected component composition, obtained according to the proposed technological scheme with the introduction of the initial alkaline components of the dispersed phase in the powdered state into the group III oil, compares favorably with the lubricant of similar component composition, obtained according to the variant with the introduction of lithium hydroxide monohydrate and calcium hydroxide in the form of aqueous solutions and without the use of components of the dispersion medium



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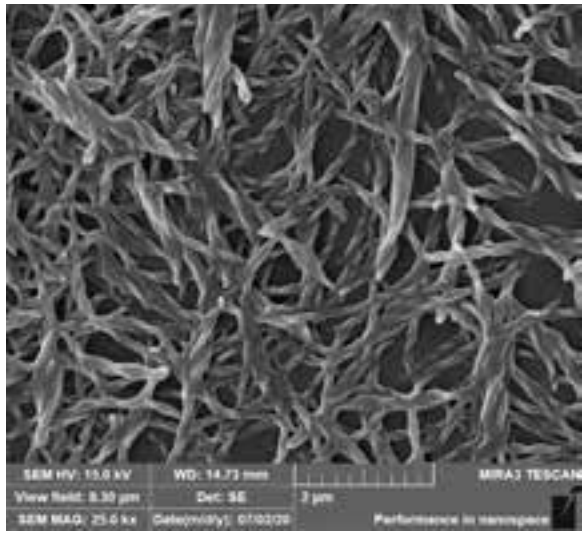

b

Figure 1 — Dispersed phase microstructure of biodegradable greases, obtained by various technological schemes:
a — variant [28]; *b* — variant [29]

at the stage of thickener formation, as well as with the use of group I mineral oil. In particular, the grease obtained according to the variant [28] thickens relatively quickly over time, and after 12 months of storage, its penetration level was $242 \cdot 10^{-1}$ mm (NLGI grade 3) at an initial value of $265 \cdot 10^{-1}$ mm (NLGI grade 2), and the ultimate shear strength at 20 °C increased from 320 to 480 Pa. The proposed technological scheme provides an increase in rheological characteristics (stabilization of the penetration index, improvement of mechanical and colloidal stability) due to the formation of a thickener with a more ordered and branched structure, while providing the required level of corrosion and antioxidant resistance of the resulting grease while maintaining the level of penetration and dropping point.

The results of four ball machine tests of biodegradable grease samples manufactured according to

Table 1 — Comparison of biodegradable grease parameters manufactured according to different technological schemes

Technology variant	Storage period, mo.	Penetration, mm·10^{-1}	Ultimate shear strength, Pa, at 20 °C	Dropping point, °C	Mass fraction of free alkali in terms of NaOH, %, not more than	Mass fraction of free organic acids mg KOH per 1 g of lubricant, not more than	Mechanical stability (change in penetration after 10,000 impacts, 10^{-1} mm)	Colloidal stability, %	Corrosion effect on metals
[28]	0	265	320	178	0.2	absent	+145	10.5	withstands
[28]	6	255	395	179	0	absent	+156	10.1	withstands
[28]	12	242	480	179	0	0.1	+175	9.2	does not withstand
[29]	0	270	315	180	0.2	absent	+60	10.8	withstands
[29]	6	270	318	180	0.2	absent	+60	10.8	withstands
[29]	12	266	330	180	0.12	absent	+65	10.4	withstands

the technology variant [29] at all test stages indicate the stability of the tribological characteristics of this lubricant (critical load P_c = 1,198–1,235 N, welding load P_w = 1,960–1,985 N, wear index D_w = 0.46–0.51 mm, load wear index LWI = 539–578 N).

The degree of biodegradability of rapeseed oil of a plastic lubricant on a mixed lithium-calcium thickener was estimated by the average degree of degradation of acids with a carbon chain length of 16 and 18, which predominate in rapeseed oil. The results of the studies are presented in Table 2.

Under the test conditions, the degree of destruction of rapeseed oil was 85 %, and the degree of plastic grease on a lithium-calcium thickener was 76 %. When the degree of degradation of rapeseed oil is 100 %, the biodegradability of the plastic lubricant on a lithium-calcium thickener is 89 %.

Development of an experimental and statistical model of the process of obtaining biodegradable greases. As a rule, the development of the formulation of lubricants and technological modes of their production is a time-consuming task, the solution of which requires significant material and time costs. One of the possible ways to reduce the cost of developing new products with the provision of the specified characteristics of its quality in the most productive way at the lowest cost is to solve optimization problems using experimental research planning methods.

From practical experience, it follows that the indicators that sufficiently fully characterize the properties of the dispersed phase and the grease as a whole can be the penetration and dropping point, the level of values of which, first of all, is affected by the amount of the dispersed phase and its composition, and from the technological modes — the heat treatment temperature of the reaction mass, which most significantly affects the nature of the processes of structure formation of the grease. Therefore, in relation to the task solution of optimizing the composition and production modes of biodegradable greases on a mixed lithium-calcium thickener, the penetration P (10^{-1}, mm) — Y_1 and the dropping point T_{dp} (°C) — Y_2 were chosen as optimization criteria, and three factors were used as optimization parameters: the content of the mixed lithium-calcium thickener in the plastic lubricant C_Z (wt.%) — x_1; the content of lithium stearate LioSt in the mixed thickener C_L (wt.%) — x_2; the heat treatment temperature of the reaction mass during the grease preparation T_{ht} (°C) — x_3. To ensure the grease biodegradability at the level of 75–80 %, the dispersion medium of the grease was a mixture of vegetable (rapeseed oil, [17]) and mineral (highly refined oil of group III according to API standard of HC-4 (NS-4) grade, TU BY 300042199.037-2015) oils in a ratio of 80:20. The methods of mathematical planning of the experiment were used to make a reasonable choice of the component composition and technological modes of obtaining a plastic lubricant, as well as to reduce the duration and volume of tests [33].

The mathematical model of the response equation from independent variables taking into account the effects of their interactions and the experimental error was presented in the form of a second degree polynomial:

$$y = b_0 + \sum_{1 \le i \le k} b_i x_i + \sum_{1 \le i \le l \le k} b_{il} x_i x_l + \sum_{1 \le i \le k} b_{ii} x_i^2, \quad (1)$$

where y is the optimization criterion; k is quantity of factors; i, l are the numbers of factors, $i \neq l$; x_i, x_l are the variable factors (optimization parameters); b_0, b_i, b_{il}, b_{ii} are the regression coefficients describing the direction and degree of influence of each of the factors on the optimization criterion.

Table 2 — Degree of degradation of the predominant fatty acids and the biodegradability of the test samples

Test sample	Degree of degradation of fatty acids, %					Degree of destruction under experimental conditions, %	Sample biodegradability, %
	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic		
Rapeseed oil	71	92	—	83	93	85	100
Lithium-calcium biodegradable grease	20	—	91	99	95	76	89

To obtain a process model in the form of a second degree polynomial, a second order non-compositional plan is implemented. The use of non-compositional plans, which provide only three levels of variation of factors (+1, 0, –1), simplifies and reduces the cost of the experiment. Non-compositional plans are characterized by the presence of a large number of zeros in the rows of the planning matrix, as a result of which the calculation of the model coefficients is significantly simplified.

Based on a priori information, the levels and intervals of variation of the factors were selected (Table 3).

In accordance with the experimental conditions (Table 4), the synthesis of biodegradable greases was carried out on a mixed lithium-calcium thickener with an assessment of the penetration values P (according to [20]) and the dropping point T_{dp} (according to [21]). These parameters most fully reflect the completeness of the processes of structural formation of the colloidal system (dispersed phase) of the grease, which significantly determines the grease quality indicators. The values of Y_1 and Y_2 are obtained as averages based on three measurements.

The second order non-compositional plan matrix for the three factors is presented in Table 4.

According to the data of experiments conducted according to the planning matrix, a model is obtained that characterizes the dependence of Y_1 on the studied process factors and is a second degree polynomial:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + \\ + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2. \quad (2)$$

The coefficients of the model were calculated using the formulas given in [33]:

$$b_0 = \frac{1}{3}\sum_{u=1}^{3} y_{0u};\ b_i = \frac{1}{8}\sum_{j=1}^{15} x_{ij}y_j;$$

$$b_{il} = \frac{1}{4}\sum_{j=1}^{15} x_{ij}x_{lj}y_j;$$

$$b_{ii} = \frac{1}{4}\sum_{j=1}^{15} x_{ij}^2 y_j - \frac{1}{16}\sum_{i=1}^{3}\sum_{j=1}^{15} x_{ij}^2 y_j - \frac{1}{6}\sum_{u=1}^{3} y_{0u}.$$

After the calculations, the following values of the coefficients of the regression equation are obtained (rounded to two decimal places):

$$b_0 = 286;\ b_1 = 11.63;\ b_2 = 8.88;\ b_3 = 1.75;$$
$$b_{12} = 7;\ b_{13} = -3.75;\ b_{23} = -7.75;$$
$$b_{11} = -11;\ b_{22} = -12;\ b_{33} = 8.75.$$

The variance $s^2\{Y_1\}$ of the optimization parameter was determined by the results of experiments in the center of the plan (see Table 4, experiments 5, 10, 15). To calculate the variance $s^2\{Y_1\}$, an auxiliary table is compiled (Table 5).

The variances characterizing the errors in determining the coefficients of the regression equation were calculated using the formulas given in [33] for the number of factors $k = 3$. The following values of the variances were obtained:

$$s^2\{b_0\} = \frac{1}{3}s^2\{Y_P\} = 19.00;\ s^2\{b_i\} = \frac{1}{8}s^2\{Y_P\} = 7.125;$$

$$s^2\{b_{il}\} = \frac{1}{4}s^2\{Y_P\} = 14.250;\ s^2\{b_{ii}\} = \frac{13}{48}s^2\{Y_P\} = 15.438.$$

Table 3 — Levels and intervals of variation of factors

Factors (parameters)	Code designation	Variation intervals	Factor levels		
			main 0	upper +1	lower –1
Thickener content C_Z, wt.%	x_1	2.0	12.0	14.0	10.0
LioSt content in thickener C_L, wt.%	x_2	10.0	70.0	80.0	60.0
Heat treatment temperature T_{ht}, °C	x_3	15.0	165	180	150

Table 4 — Planning matrix and experiment results

Experiment number	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	x_{12}	x_{22}	x_{32}	Y_1, penetration P, 10^{-1} mm	Y_2, dropping point T_{dp},°C
1	+	+	+	0	+	0	0	+	+	0	300	199
2	+	+	–	0	–	0	0	+	+	0	260	192
3	+	–	+	0	–	0	0	+	+	0	252	184
4	+	–	–	0	+	0	0	+	+	0	240	195
5	+	0	0	0	0	0	0	0	0	0	279	202
6	+	+	0	+	0	+	0	+	0	+	295	200
7	+	+	0	–	0	–	0	+	0	+	285	194
8	+	–	0	+	0	–	0	+	0	+	290	186
9	+	–	0	–	0	+	0	+	0	+	265	189
10	+	0	0	0	0	0	0	0	0	0	285	205
11	+	0	+	+	0	0	+	0	+	+	290	197
12	+	0	+	–	0	0	–	0	+	+	285	189
13	+	0	–	+	0	0	–	0	+	+	265	198
14	+	0	–	–	0	0	+	0	+	+	291	183
15	+	0	0	0	0	0	0	0	0	0	294	209

To check the significance of the model coefficients, let us find their confidence intervals. The confidence interval Δb_0 of the coefficient b_0 is found by the expression:

$$\Delta b_0 = \pm t_T s\{b_0\} = \pm 8.892,$$

where t_T is the tabular value of the Student's t-test; with the number of degrees of freedom f equal to 30 and a 5 % significance level $t_T = 2.04$.

$$f = (n-1)\cdot N = (3-1)\cdot 15 = 30,$$

where N is the number of experiments in the planning matrix; n is the number of parallel experiments.

Similarly, we determine the confidence intervals of the coefficients b_i, b_{il}, b_{ii}:

$$\Delta b_i = \pm t_T\, s\{b_i\} = \pm 5.445;$$
$$\Delta b_{il} = \pm t_T\, s\{b_{il}\} = \pm 7.701;$$
$$\Delta b_{ii} = \pm t_T\, s\{b_{ii}\} = \pm 8.015.$$

The coefficient is significant if its absolute value is greater than the confidence interval. The coefficients b_3, b_{12}, b_{13} are smaller than the confidence interval, so it can be considered statistically insignificant and excluded from the regression equation. Then the regression equation (2) gets the form:

$$Y_1 = 286 + 11.63x_1 + 8.88x_2 + 7.75x_2x_3 - \\ - 11x_1^2 - 12x_2^2 + 8.75x_3^2. \quad (3)$$

The adequacy of the obtained model is checked by the Fischer's F-test. To calculate the variance of s^2_{ad} adequacy, we find the sum of the s_R squared deviations of the calculated values of $\hat{Y}_1$ from the experimental Y_1 at all points of the plan (Table 6). The calculated values of $\hat{Y}_1$ are determined by the expression (3), $s_E = 114$ (see Table 5).

Let us find the variance:

$$s^2_{ad} = \frac{s_R - s_E}{N - k' - (n_0 - 1)} = \frac{897.75 - 114}{15 - 7 - (3-1)} = 130.625,$$

where N is the total number of experiments; k' is the number of coefficients of the approximating polynomial (the number of significant factors); n_0 is the number of experiments in the center of the plan.

Variance $s^2\{Y_1\} = 57$ (see Table 5), therefore, the calculated value of the F-test is:

$$F_P = \frac{s^2_{ad}}{s^2\{Y_1\}} = 2.29.$$

The table value of the F-test at a 5 % significance level and the number of degrees of freedom for the larger variance $m_1 = N - k' - n_0 + 1 = 6$, the smaller variance $m_2 = n_0 - 1 = 2$, $F_T = 19.37$. Since $F_P < F_T$, the resulting model (3) is adequate at a 5 % significance level.

The equation analysis (3) shows that within the established intervals of factor variation, an increase in factor x_1 has a greater effect on the increase in the penetration index P than in factors x_2 and x_3, but due to the presence of quadratic terms in equation (3), this dependence is nonlinear, which is most strongly manifested through factor x_1.

For the convenience of interpreting the results obtained and using the equation (3) for practical calculations, it is necessary to switch from the encoded values (x_1, x_2, x_3) of the factors to the natural values (C_Z, C_L, T_{ht}). To do this, we used the following formulas:

$$x_1 = \frac{C_Z - C_{Z0}}{\Delta C_Z}; \quad x_2 = \frac{C_L - C_{L0}}{\Delta C_L}; \quad x_3 = \frac{T_{ht} - T_{ht0}}{\Delta T_{ht}},$$

where C_{Z0}, C_{L0}, T_{ht0} are the natural values of the factors at the main levels; ΔC_Z, ΔC_L, ΔT_{ht} are the values of the variation intervals.

Thus, according to Table 3,

$$x_1 = \frac{C_Z - 12}{2}; \quad x_2 = \frac{C_L - 70}{10}; \quad x_3 = \frac{T_{ht} - 165}{15}.$$

Taking into account the transition to the natural values of the factors, the regression equation (3) will take the form:

$$Y_1(P) = 386 + 6.5 \cdot C_Z + 0.4 \cdot C_L - \\ - 0.0067 \cdot C_L \cdot T_{ht} - 1.94 \cdot T_{ht} - 0.25 \cdot C_Z^2 - \\ - 0.01 \cdot C_L^2 + 0.0045 \cdot T_{ht}^2. \quad (4)$$

Similarly, the regression equation for the dropping point $Y_2(T_{dp})$ is obtained:

$$Y_2 = 205.33 + 3.88 \cdot x_1 + 3.25 \cdot x_3 + \\ + 4.50 \cdot x_1 \cdot x_2 - 6.17 \cdot x_1^2 - 6.67 \cdot x_2^2 - 6.92 \cdot x_3^2. \quad (5)$$

The resulting model is adequate at a 5 % significance level, since

$$F_P = \frac{s^2_{ad}}{s^2\{Y_2\}} = 2.04 < F_T = 19.37.$$

After switching from the encoded values (x_1, x_2, x_3) of the factors to the natural values (C_Z, C_L, T_{ht}), the equation (5) will take the form:

$$Y_2(T_{dp}) = 8.33 + 3 \cdot C_Z + 0.9 \cdot C_L + \\ + 0.05 \cdot C_Z \cdot C_L + 1.47 \cdot T_{ht} - 0.25 \cdot C_Z^2 - \\ - 0.01 \cdot C_L^2 - 0.0045 \cdot T_{ht}^2. \quad (6)$$

Table 5 — Auxiliary table for calculating $s^2\{Y_1\}$

Experiment number in the center of the plan	Y_1	$\bar{Y}_1$	$Y_1 - \bar{Y}_1$	$(Y_1 - \bar{Y}_1)^2$
5	279.00	286.00	–7.00	49.00
10	285.00		–1.00	1.00
15	294.00		8.00	64.00
$s^2\{Y_1\} = \frac{s_E}{n_0 - 1} = \frac{114.00}{3-1} = 57.00$				$s_E = \sum (Y_1 - \bar{Y}_1)^2 = 114.00$

Table 6 — Auxiliary table for calculating s_R

Experiment number	Y_1	$\hat{Y}_1$	$Y_1 - \hat{Y}_1$	$(Y_1 - \hat{Y}_1)^2$
1	300.00	290.50	9.50	90.25
2	260.00	258.75	1.25	1.56
3	252.00	253.25	–1.25	1.56
4	240.00	249.50	–9.50	90.25
5	279.00	286.00	–7.00	49.00
6	295.00	291.63	3.38	11.39
7	285.00	299.13	–14.13	199.52
8	290.00	275.88	14.13	199.52
9	265.00	268.38	–3.38	11.39
10	285.00	286.00	–1.00	1.00
11	290.00	299.38	–9.38	87.89
12	285.00	283.88	1.13	1.27
13	265.00	266.13	–1.13	1.27
14	291.00	281.63	9.38	87.89
15	294.00	286.00	8.00	64.00
$s_R = \sum\left(Y_l - \hat{Y}_l\right)^2 = 897.75$				

The analysis of the equation (6) shows that within the established intervals of factor variation, an increase in factor x_1 also has a greater effect on the increase in the dropping point T_{dp} than factors x_2 and x_3, but due to the presence of quadratic terms in the equation (6), this dependence is nonlinear, which is most strongly manifested through factor x_1.

The regression equations (4) and (6) can be used to select the formulation and technological modes for the production of greases that provide optimal values of penetration and dropping points, depending on the factors under study (C_Z, C_L, T_{ht}). Figures 2–7 show the graphical dependences of the penetration and dropping point on the studied factors obtained using the equations (4) and (6). When constructing the response surface (SigmaPlot 12 program), the variation of two factors was chosen with a fixed third factor.

Figures 2–7 show that the main influencing factor on the penetration value is the content of the thickener C_Z, then the content of lithium stearate LioSt in the thickener C_L and the heat treatment temperature T_{ht}. The highest penetration values (at the level of P = (285–290)·10^{-1} mm) are provided when the content of the mixed thickener in the grease C_Z = 12.5–13.5 wt.%, the content of lithium stearate LioSt in it in the amount of C_L= 70–80 wt.% and at the heat treatment temperature T_{ht} = 165–180 °C, and the highest values for the dropping point at the level of the values T_{dp} = 200–206 °C are obtained in the case of the content of the mixed thickener in the range C_Z = 12.5–14 wt.% in the presence of lithium stearate LioSt in the amount of C_L = 72–80 wt.% and under the condition of heat treatment of the reaction mass in the temperature range T_{ht} = 165–175 °C.

If it is necessary to obtain a biodegradable lithium-calcium lubricant with penetration and dropping point values that meet the requirements stipulated in the technical specifications of TU BY 190410065.021-2020 "Biodegradable plastic lubricant "OIMOL CL BIO" (penetration (265–295)·10^{-1} mm, dropping point not

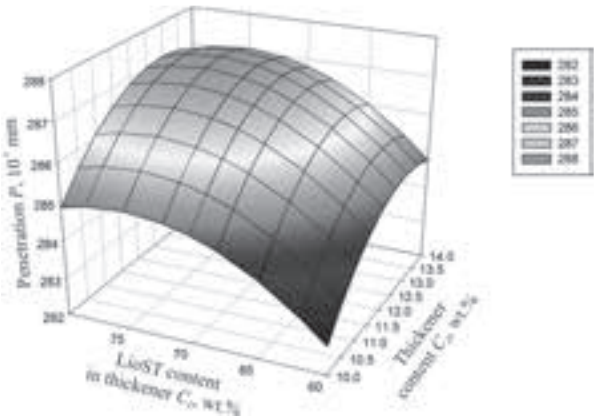

Figure 2 — Dependence of the penetration P on the content of the mixed thickener C_Z and the content of lithium stearate LioSt in the thickener C_L with the heat treatment temperature of the reaction mass T_{ht} = 165 °C

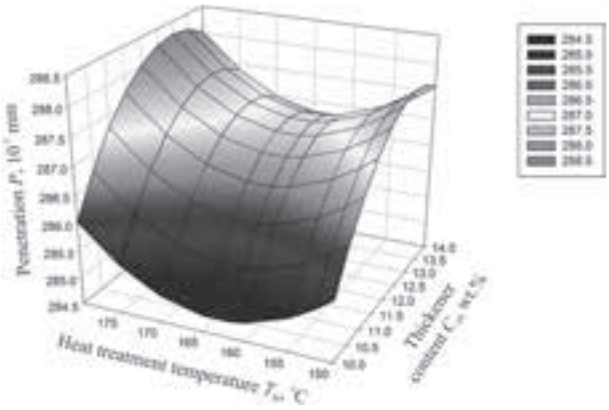

Figure 3 — Dependence of the penetration P on the content of the mixed thickener C_Z and the heat treatment temperature of the reaction mass T_{ht} with the content of lithium stearate LioSt in the thickener C_L = 70 wt.%

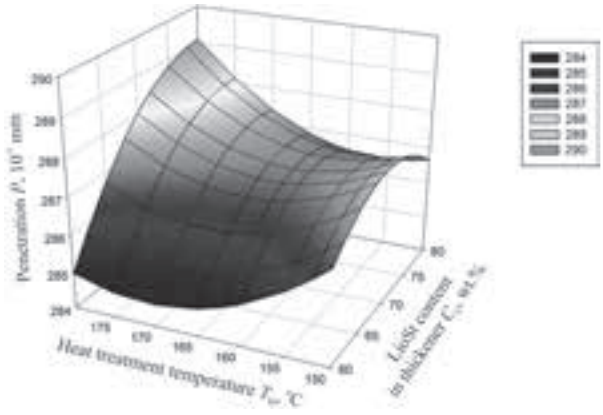

Figure 4 — Dependence of the penetration P on the content of lithium stearate LioSt in the mixed thickener C_L and the heat treatment temperature of the reaction mass T_{ht} with the content of the mixed thickener C_Z = 12 wt.%

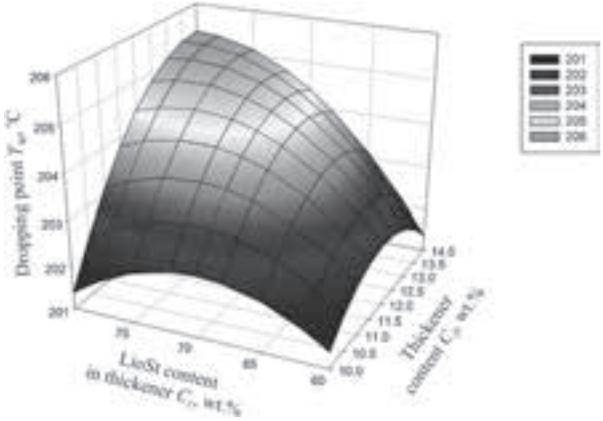

Figure 5 — Dependence of the dropping point T_{dp} on the content of the mixed thickener C_Z and the content of lithium stearate LioSt in the thickener C_L with the heat treatment temperature of the reaction mass T_{ht} = 165 °C

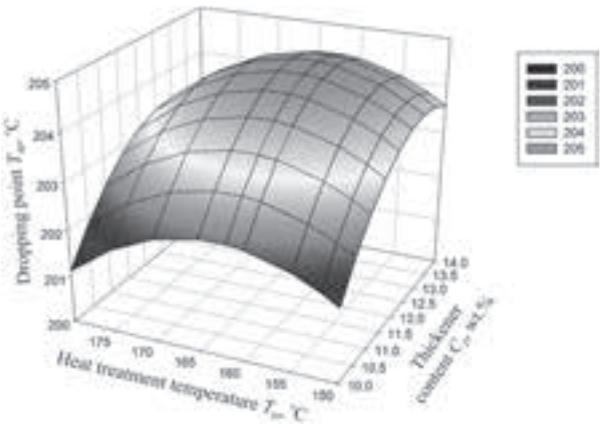

Figure 6 — Dependence of the dropping point T_{dp} on the content of the mixed thickener C_Z and the heat treatment temperature of the reaction mass T_{ht} with the content of lithium stearate LioSt in the thickener C_L = 70 wt.%

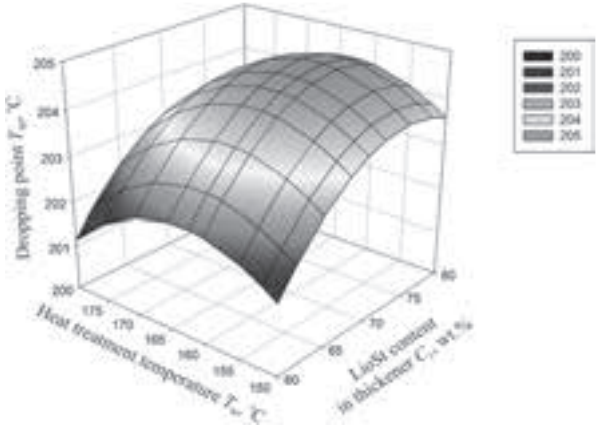

Figure 7 — Dependence of the dropping point T_{dp} on the content of lithium stearate LioSt in the thickener C_L and the heat treatment temperature of the reaction mass T_{ht} with the content of the mixed thickener C_Z = 12 wt.%

less than 200 °C), the parameters of the formulation and technological modes laid down in the experimental and statistical model should be within the limits: the content of the mixed thickener C_Z = 11–12 wt.%; lithium stearate LioSt in it C_L = 70–74 wt.%, the heat treatment temperature of the reaction mass T_{ht} = 165–170 °C.

Table 7 shows the values of the parameters of the technically optimal version of the synthesis process of biodegradable grease on a mixed lithium-calcium thickener, which corresponded to the conditions for obtaining the lubricant when checking the adequacy of the developed mathematical model.

The rheological properties (penetration and dropping point) of a biodegradable plastic lubricant based on a mixed lithium-calcium thickener obtained by checking the adequacy of the experimental and statistical mathematical model developed are shown in Table 8.

The analysis of the data given in Table 8 indicates the adequacy of the developed experimental and statistical mathematical model of the process of obtaining biodegradable grease on a mixed lithium-calcium thickener.

Thus, based on the results of computational and experimental modeling, it can be concluded that in order to obtain a biodegradable plastic lubricant on a lithium-calcium thickener with the values of penetration and dropping point of the plastic lubricant that meet the requirements of the technical specifications of TU BY 190410065.021-2020 “Biodegradable plastic lubricant “OIMOL CL BIO”, the component composi-

Table 7 — Parameters of the technically optimal variant of the synthesis process of biodegradable grease on the mixed lithium-calcium thickener

Parameter name	Values of process parameters	
	calculated	actual
Content of mixed thickener in lubricant C_Z, wt.%	11.0±0.5	11.0
Content of lithium stearate LioSt in mixed thickener C_L, wt.%	72±2	72.0
Reaction mass heat treatment temperature T_{ht}, °C	167.5±2.5	168–170

Table 8 — Rheological properties of biodegradable grease based on the mixed lithium-calcium thickener

Quality indicator	Value of indicators		
	required level	calculated values	actual values
Penetration P, 10^{-1} mm	265–295	275–290	282–287
Dropping point T_{dp}, °C	not more than 200	200–205	200–203

tion and technological modes of the process of obtaining the lubricant must correspond to the following ranges: the content of the mixed thickener in the lubricant C_Z is 11.0±0.5 wt.%; the content of lithium stearate LioSt in the mixed thickener C_L is 72±2 wt.%; the temperature of heat treatment of the reaction mass T_{ht} is 167.5±2.5 °C.

Conclusion. Thus, it can be concluded that the selected component composition of the dispersion medium (a mixture of rapeseed oil and highly refined oil of group III according to the API standard of the HC-4 (NS-4) brand in the ratio of 4:1) and the proposed version of the technological scheme for the synthesis of plastic grease on a mixed lithium-calcium thickener with the introduction of the initial alkaline components of the dispersed phase in a powdery state, brought to a nanoscale level, made it possible to obtain a lubricant characterized by a high level of colloidal and mechanical stability and other rheological and tribological characteristics, with a good degree of preservation of properties during the storage of the lubricant (at least up to 1 year) and with the required level of its biodegradability (at least 80 %).

Using a computational and experimental mathematical model, it was established that to obtain a biodegradable plastic lubricant based on a lithium-calcium thickener that meets the requirements of the technical specifications of TU BY 190410065.021-2020 "Biodegradable plastic lubricant "OIMOL CL BIO", with penetration values in the range of (265–295)·10^{-1} mm and a dropping point of not less than 200 °C, the content of the mixed thickener in the lubricant should be 11.0±0.5 wt.% with the amount of lithium stearate LioSt in it 72±2 wt.%, and the heat treatment temperature of the reaction mass should be at the level of 167.5±2.5 °C.

The developed general technical grease OIMOL CL BIO is an environmentally friendly lubricant designed for the lubrication of low- and medium-load friction units of various machines and mechanisms operating in the temperature range from –30 to +120 °C in conditions where there are increased requirements for environmental protection and there is a possibility of lubricants entering the soil or water bodies (forestry, agriculture and utilities, railway and water transport, etc.).

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ОТРАБОТКА СПОСОБА И ОПТИМИЗАЦИЯ СОСТАВА И РЕЖИМОВ ПОЛУЧЕНИЯ БИОРАЗЛАГАЕМОЙ ПЛАСТИЧНОЙ СМАЗКИ С ЛИТИЙ-КАЛЬЦИЕВЫМ ЗАГУСТИТЕЛЕМ

Отмечено, что разработка биоразлагаемых смазочных материалов является неотъемлемой частью развития современной «зеленой» экономики. Описаны отличительные особенности предложенного способа получения биоразлагаемого пластичного смазочного материала на смешанном литий-кальциевом загустителе, предусматривающего введение в реакционную массу щелочных исходных компонентов дисперсной фазы (моногидрата гидроксида лития и гидроксида кальция) не в виде их водных растворов, а в порошкообразном состоянии и исключение длительного воздействия воды и высоких температур на компонент дисперсионной среды растительного происхождения (рапсовое масло) в процессе синтеза смазки. Наряду с этим предложено использовать в качестве минерального компонента дисперсионной среды высокоочищенное масло III группы по стандарту API (American Petroleum Institute), что в совокупности обуславливает более высокую стабильность реологических и трибологических характеристик смазочного материала (в тече-

ние не менее 12 месяцев) при заданном уровне биоразлагаемости. Разработана экспериментально-статистическая математическая модель процесса получения биоразлагаемой пластичной литий-кальциевой смазки, позволяющая определять параметры компонентного состава (содержание смешанного литий-кальциевого загустителя в смазке и содержание стеарата лития в смешанном загустителе) и режимов синтеза (температуру термообработки реакционной массы) для достижения заданного уровня основных характеристик готовой пластичной смазки (пенетрация, температура каплепадения) при обеспечении ее биоразлагаемости не ниже 80 %.

Ключевые слова: *пластичный смазочный материал, дисперсионная среда, смесь растительного и минерального масел, дисперсная фаза, литий-кальциевый загуститель, реологические и трибологические свойства, биоразлагаемость*

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