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Section 1. Biology

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Special features of formation of the dimensional structure and life strategy of coenopopulations of *Polygonatum multiflorum (L.) All.* in the ecotopes of Precarpathians (Western Ukraine)

Abstract: The article provides the analysis on the special features of the dimensional structure and the character of the life strategy formation of the coenopopulations of *Polygonatum multiflorum (L.) All.* The studies were conducted in different types of ecotopes in Precarpathians in order to assess the ecological plasticity of the species' coenopopulations and to determine their adaptive capacity and resistance under heterogeneous environmental conditions.

Keywords: *Polygonatum multiflorum (L.) All.*, coenopopulation, ecotope, Precarpathians, dimensional structure, life strategy.

Introduction

The condition for objective cognition of structural-dynamic organization of natural phytocenosis and their ecologically substantiated management is the study of populational-ecological peculiarities of species that form their structure. In Precarpathians the representatives of aboriginal boreal-nemoral flora represent a significant scientific interest, an honorable place among which belongs to *Polygonatum multiflorum (L.) All.* The researches of populational-ecological peculiarities of this species under the conditions of natural and anthropogenically modified ecotopes of Precarpathians have important theoretical and practical value, as they serve as a prerequisite for solving a number of problems of sozological and resource character, and for determination of the populations' adaptive capacity.

The objective of this work was to investigate the dimensional structure and the concerned life strategy of *Polygonatum multiflorum (L.) All.* in the ecotopes of Precarpathians, to analyze their bioindicative prospects and adaptive significance for the populations.

Materials and methods

The coenopopulations of *Polygonatum multiflorum (L.) All.* were studied in different ecotopes of Precarpathians during the vegetation periods 2007–2016. In detection of ecotopes we were guided by all-European classification according to the EUNIS-scheme, additionally performing a conditional division of the detected types of ecotopes into unchanged (G4.6 – forest ecotopes and E5.21 – margin ecotopes), slightly changed (E2.11 – pastoral ecotopes) and greatly changed (G5.8 – timber blocking and J.1 – ecotopes that are intended for building). Experimental plots are located within 4 administrative regions of Western Ukraine: Ivano-Frankovsk, Lviv, Ternopil and Chernivtsi, where the growth areas of *Polygonatum multiflorum (L.) All.* are recorded according to the literature data and herbarial information. Under the predominant aggregative (mosaic) distribution of specimens of the species, the experimental plots were laid by the transect method, adhering to the optimal sample size (25 specimens); under the uniform distribution — they were laid at the same distance from each other. The size of the accountable plot was $\approx 1\,m^2$.

The dimensional structure of coenopopulations was analyzed, and their life strategies were evaluated. The prospectivity for application of the concerned population parameters as phytoindicative features and as markers of the populations's ecological status was determined.

The dimensional structure of cenopopulations was estimated by determination of the main morphometric parameters of plants. The average length and mass of the aboveground and underground parts of plants, average leaf length and width, number of leaves and flowers on the plant, number of fruits, their diameter and mass were determined.

Evaluation of the coenopopulations' life strategies was carried out on the basis of comparison of the efforts, which were spent by plants on vitality maintenance and reproduction with calculation of corresponding ratings for each of the considered morphometric parameters of vegetative and generative organs. Then the integrated indexes were determined and compared with each other according to the proven methodology. Integral rating of vital forces (Irvf) was calculated as the amount of efforts for vitality maintainance and reproduction.

Statistical analysis of the results was performed by variational-statistical method. The statistical significance of the differences between the obtained experimental data and the background data was estimated with the help of the Student's t-test. The null hypothesis was discarded at $p \leq 0,05$. All calculations were performed with MS Excel 2003.

Results and discussion

The dimensional differentiation of specimens is one of the main characteristics of coenopopulations and characterizes peculiarities of the processes inside the population, reflects the possibilities for realization of the species's life potential under specific environmental conditions, comfortability of natural conditions for the population's existence. The obtained results indicate a considerable variability of analyzed morphological parameters of generative and vegetative spheres of specimens of *Polygonatum multiflorum (L.) All.* in the ecotopes with different ecological conditions (Table 1).

The maximum absolute values of morphometric parameters of vegetative and generative organs of *Polygonatum multiflorum* (L.) All. were established for coenopopulations of the ecotopes that are intended for building. A significant difference with the background population ($p < 0.05$) was revealed through the height and mass of aboveground part, length and mass of the underground part and number of fruits. Low values of morphometric parameters are typical for the specimens of coenopopulations of a pastoral ecotope. The difference between average morphometric parameters of coenopopulation's reference samples fluctuate in the range from 12% (average leaf length) to 55% (mass of the underground part).

Table 1. – Morphometric parameters of vegetative and generative organs of
Polygonatum multiflorum (L.) All. in the ecotopes of Precarpathians

	Ecotope type / Parameter	Unchanged ecotopes		Slightly changed ecotopes	Greatly changed ecotopes	
		Forest (G4.6)	Margin (E5.21)	Pastoral (E2.11)	Intended for building (J1)	Ecotope on timber blockings (G5.8)
1	Height of aboveground part, cm	53,3 ± 3,67	59,1 ± 3,01	43,94 ± 3,92	62,4 ± 3,24*	51,42 ± 3,68
2	Length of underground part, cm	9,8 ± 054	12,31 ± 0,67	7,02 ± 0,66	13,52 ± 0,71*	10,52 ± 0,78
3	Average leaf length, cm	8,9 ± 0,52	9,75 ± 0,56	7,84 ± 0,42	9,8 ± 0,38	9,40 ± 0,54
4	Average leaf width, cm	3,1 ± 0,22	3,37 ± 0,27	2,08 ± 0,24	3,5 ± 0,33	2,90 ± 0,33
5	Amount of leaves, pieces	13,4 ± 0,81	18,54 ± 1,05	8,58 ± 1,01	17,8 ± 1,21	12,0 ± 0,98
6	Amount of flowers, pieces	20,9 ± 1,23	24,7 ± 1,84	18,0 ± 0,92	25,2 ± 1,78	23,1 ± 1,05
7	Amount of fruits, pieces	16,4 ± 0,85	21,4 ± 1,02	12,9 ± 1,1	23,9 ± 0,98*	14,5 ± 0,78
8	Diameter of fruits, cm	0,9 ± 0,052	1,0 ± 0,048	0,7 ± 0,037	0,90 ± 0,052	0,82 ± 0,056
9	Mass of aboveground part, g	1,5 ± 0,085	1,5 ± 0,084	1,3 ± 0,67	1,78 ± 0,085*	1,42 ± 0,33*
10	Mass of underground part, g	2,9 ± 0,18	3,0 ± 0,35	1,3 ± 0,33	3,6 ± 0,33*	2,8 ± 0,58*
11	Mass of fruits, g	2,9 ± 0,15	3,4 ± 0,35	1,4 ± 0,09	3,3 ± 0,35	2,4 ± 0,33

* – the difference is authentic with the background (forest ecotope of Halytsky National Nature Park, Ivano-Frankivsk Oblast)

The most stable morphometric indicators in all investigated coenopopulations are the average leaf length and mass of the aboveground part; the most labile indicators – the mass of the underground part and fruits.

The distribution of the fixed amount of energy between vegetative and generative spheres reflects the type of populations' life strategy and serves as an informative diagnostic marker of their status under the conditions of a particular ecotope. The results of quantitative determination of life strategies of the studied coenopopulations of *Polygonatum multiflorum (L.) All.* are presented in the table 2.

Table 2. – Ratings of vital forces and types of coenopopulations' strategies of
Polygonatum multiflorum (L.) All. in the ecotopes of Precarpathians

Index of ecotope	Rating of efforts for vitality maintenance	Rating of efforts for reproduction	Integral rating of vital forces	Type of life strategy
G4.6	0,52	0,63	1,15	R
E5.21	0,76	0,83	1,59	R
E2.11	0,00	0,00	0,00	R
J1	0,99	0,98	1,97	K
G5.8	0,44	0,47	0,91	R

In *Polygonatum multiflorum (L.) All* the energy consumption on the development of vegetative and generative spheres are alike in all studied ecosystems. Competitive type of strategy is typical for coenopopulations of the ecotopes that are intended for building. The energy consumption on reproduction in all other coenopopulations is higher than on vitality maintenance. The integral rating of vital forces of coenopopulations decreases in the sequential row: ecotopes intended for building → forest margins → forest ecotopes → ecotopes on timber blockings → pasture, which indicates the increase in efforts of the complex of edapho-climatic and anthropogenic factors in the similar row of investigated ecotopes. At the same time, coenopopulations of *Polygonatum multiflorum (L.) All.* demonstrate significant plasticity and good adaptive ability under different environmental conditions, including anthropogenically changed, which is evidenced by the preservation of the integral rating of vital forces of most studied populations at the level of high ($1 < Irvf < 1.5$) and very high ($Irvf > 1, 5$) values. The formation of ecotopes, which are intended for building, by coenopopulations of K-strategy of survival with $Irvf > 1.5$ allows to consider the ecotope conditions as reference for the given species.

Conclusions

The coenopopulations of *Polygonatum multiflorum (L.) All.* are characterized by the variability of morphometric parameters of the species in ecotopes with different environmental conditions and degrees of anthropogenic transformation. The most stable morphometric features in coenopopulations of all studied ecotopes are the average leaf length and mass of the aboveground part, the most labile ones – mass of the underground part and fruits. The considered morphometric parameters can serve as informative markers of comfortability of living conditions of the coenopopulations of *Polygonatum multiflorum (L.) All.*

Competitive type of strategy is typical for coenopopulations of the ecotopes intended for building; all other populations are characterized by ruderal type. Integral rating of vital forces decreases in the sequential row: ecotopes intended for building → margins → forest ecotopes → ecotopes on the timber blocking → pasture.

Plasticity of morphological parameters and ability to redistribute energy consumption between the generative and vegetative spheres indicate a good adaptive ability of coenopopulations of *Polygonatum multiflorum (L.) All.*

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Section 2. Information technology

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Diagnosis of multiple-output microprocessor devices and methods of reference signature calculation

Abstract: Issues of diagnosis and approaches of using of signature analysis for diagnosis of multiple-output digital devices are considered in this paper. Methods of signatures calculation for signature analysis are given. Algorithm and software for automation of reference digital signature calculation is given.

Keywords: Microprocessor sets, data communication equipment, large scale integration, very large scale integration, technical replacement element, signature analyzer, multichannel signature analyzer.

The transition to the widespread use of (MPS) in the modern data communication equipment (DCE) has created a number of serious problems associated with the processes of diagnosis.

Modern DCE has a wide range of digital cards which use various element bases. The widespread use of LSI (large scale integration), VLSI () and MPS in the DCE have established together with the indisputable advantages a number of serious problems in their operational services primarily related to the processes of monitoring and fault diagnosis [1–3].

Improving the technical and operational characteristics of the complex DCE-based LSI, VLSI and MPS is inextricably linked with the development of techniques and methods of diagnosis with the need to analyze multiple-output digital device signatures.

Of the many areas of diagnostics features the latest combination of test and functional diagnosis, in which the means of functional diagnostics assign a task only prompt discovery of the fault, and the search for the failed component is carried out by the means of test diagnosis. In terms of the DCE exploitation, troubleshooting control sequence is as follows: DCE, unit (subunit), a technical replacement element (TRE), the individual integrated circuits and electric radio elements.

One of the microprocessor systems strong external diagnosis tools is a signature analyzer (SA) [1–3]. The principle of operation is based on the signature analysis, i. e. compression of long sequences of a 4-digit 16 hexadecimal signatures. Physically, this method is implemented in a linear shift register with feedback signals which are summed by modulo 2 with the input sequence.

The problem of multiple-output analysis of digital devices and the process of testing is to identify a fault circuit on its output reactions. The distinguishing feature of this type of analysis is the need to study a sufficiently large number of output responses, therefore, the use of traditional methods of compact testing which are used for single-output digital circuits, in this case, does not allow us to obtain the desired effect. Analysis of n – digital output circuit monophonic signature analyzer (SA) increases the time required for circuit analysis by n times or the hardware required to implement the n signature analyzers. Therefore, in practice multichannel signature analyzer often is used. (MSA) The signature of the multichannel signature analyzer S (y) is uniquely determined by the number of n investigated schemes outputs. Therefore, as n increases the complexity of the compression device and the number of bits used to represent the signature S(y), takes almost an invalid size.

An important parameter of the signature analysis is the set of reference signatures, which is determined in advance for correct digital device. The need to establish methods for the calculation of signatures associated with the need to automate the production of dictionaries (tables) reference signatures, since their creation by measuring the signature is quite time consuming. Therefore, the basic document of signature analysis is the standard signature dictionary, which defines the troubleshooting algorithm.

At present, there are various theoretical methods for calculating the reference signatures [2–5].

Calculation method of the reference signatures based on the analysis of the SA

As you know, the essence of the SA is that the data sequences from the node of the properly functioning circuit in the test mode are set in accordance with a specific signature. During the next test of this scheme, operator with a signature analyzer measures at different points in the digital circuit unit and compares them with before taken reference signatures in the documents. The principle of operation is based on the SA method of signature analysis, ie compression of long sequences in the four-digit hexadecimal signature. Physically, this method is implemented in a linear shift register with feedback signals, which are summed by modulo two with the input sequence. As polynomial irreducible polynomial is used:

$$P(X) = x^{16} + x^{12} + x^9 + x^7 + 1$$

Signatures are reproduced, usually in the alphabet consisting of six to ten digits and letters: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, A, C, F, H, P, U. Each binary sequence has its own signature.

0000 — "0" 0100 — "4" 1000 — "8" 1100 — "F"
0001 — "1" 0101 — "5" 1001 — "9" 1101 — "H"
0010 — "2" 0110 — "6" 1010 — "A" 1110 — "P"
0011 — "3" 0111 — "7" 1011 — "C" 1111 — "U"

The signature is generated using a shift register with feedback logic $P(x) = x^{16} + x^{12} + x^9 + x^7 + 1$, at which input is modulo two adder. Assume that during the connection of the probe parser to any reference point, it occurred 20 – bit sequence of ones and zeros having the form: 11111100000111111111. This input sequence is added by modulo 2 to the contents of the cells 7, 9, 12 and 16 of the shift register. After 20 cycles of the scheme in the register will be 16-bit combination is 1101100101010011, which as a result of the division into four four-digit alphanumeric combinations corresponds to – the digital signature of H953.

A simplified method for calculating the reference signatures

As noted previously, the method of the SA is to compress the output responses of the subjects of electronic components with the help of the shift register with logic feedback in short words — the signature. Implementation principle of the SA generally is based on the mathematical ratios, similar to those used in the formation of the cyclic codes. However, due to the fact that the practical scheme of the divider is made on multi-input adders modulo-2 differs from that used divider cyclic code, the contents of the shift register and the result of division of SA, F(x) on P(X) is not the same. It is known that the residue obtained in the shift register is of the form R(x) = = x15 + x14 + x12 + x11 + x8 + x6 + x4 + x + 1, and the remainder after dividing the F(X) at F′(x) has the form: x15 + x14 + x12 + x11 + x7.

In this regard, it is necessary to analyze not the remainder of the division, but the quotient. In accordance with this method, a signature is calculated by multiplying the input polynomial F(X) by a monomial XR and dividing this product by the inverse generator polynomial

$$\frac{F(X)X^r}{P'(X)} = Q(X) + \frac{R(X)}{P'(X)} \qquad (1)$$

In this case, the quotient has the same degree as F (X), and the signature is the last r bits.

$$r_c(X) = [Q(X)] \bmod 2^r$$

Consider the example of a theoretical calculation of the signature for this method for similar to the previously considered the input sequence. Multiplying the input polynomial F (X) by a monomial X16 obtain:

$$F(X)\,X^{16} = x^{35} + x^{34} + x^{33} + x^{32} + x^{31} + x^{30} + x^{29} + x^{23} + $$
$$+ x^{22} + x^{21} + x^{20} + x^{19} + + x^{18} + X^{17} + x^{16}.$$

We divide this polynomial by a polynomial inverse $P'(X) = x^{16} + x^9 + x^7 + x^4 + 1$.

As a result, we obtain quotient, $Q(X) = x^{19} + x^{18} + x^{17} + x^{16} + x^{15} + x^{14} + x^{13} + x^{12} + x^{11} + x^8 + x^6 + x^4 + x + 1$. And the remainder, $R(X) = x^{15} + x^{13} + x^{10} + x^9 + x^8 + x^7 + x^6 + x^2 + x$

Transforming $Q(X)$ into the binary form we obtain $Q(X) = 11111100100101010011$

The last 16 bits of the method are the signature, i. e.

1101100101010011 corresponds to the signature of H953.

Method for determination of signatures based on modeling the signature analyzer

The simulation program of the signature method diagnosis for digital devices SIGNATURA is designed to indicate the process of forming a digital signature for the diagnosis of the device [5]. The program simulates the process of passing through a sequence of digital logic circuit consisting of a shift register and modulo-2 adder. After the simulation, the program produces results – a digital signature in the form of a code is displayed on the seven-segment display.

The program requires no installation, and is started by running the application signatura.exe. When you run the program, a window appears.

The program window contains the image of the simulated circuit at the top, and at the bottom — the controls.

The sequence of operation of the program is as follows:

– Set the bit shift register;
– Set the level of the polynomial;
– Introduce an input sequence;
– If necessary, set the interval for acceleration/deceleration process;
– Press the "Start" button.

When you click on "Start" to the input of the adder modulo 2 an input sequence starts being supplied. The levels of the input sequence pass through logic circuit and are stored in the shift register.

When all the bits of the input sequence pass through the logic circuit appears on the screen a digital signature, which is a code for the seven-segment display (Figure 1).
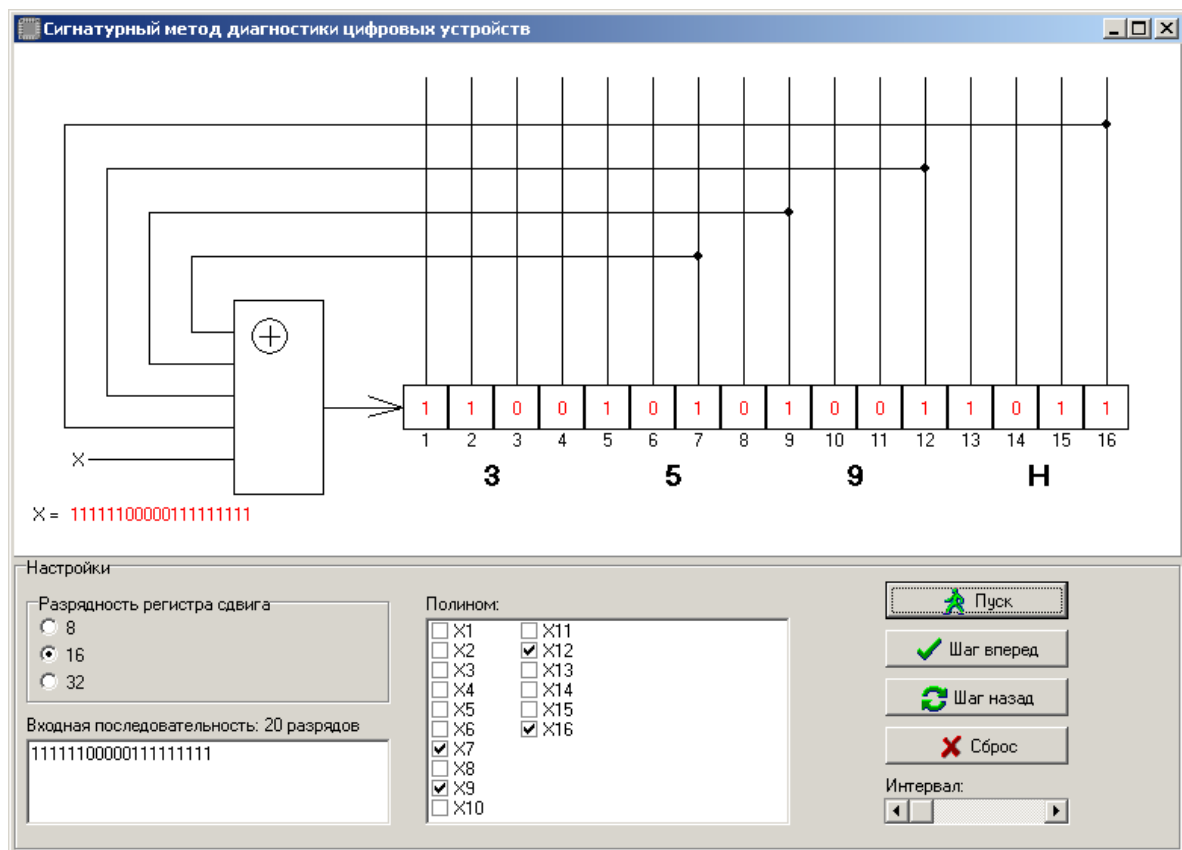
Figure 1. The digital signature after the process finished

Each character of the signature is displayed under the corresponding four bits of the shift register. To the hexadecimal register corresponds a four-character signature, to the eight-bit – a two-character, for the thirty-bit – an eight character signature corresponds.

Thus, the following results were obtained:

Proposed the simplified method of calculating the reference signatures, which has lower complexity, and free from shortcomings that are inherent in the known theoretical methods for calculating the reference signatures.

In order to automate the definition of the reference signatures a new algorithm and simulation program of the signature method diagnosis for digital devices are developed.

The developed software is compatible with operating systems Microsoft Windows NT/2000/XP/2003/7.

Conclusion

1. Analysis of the characteristics of existing control and diagnostic tools showed that practically only methods and means of signature analysis is ready to use in the maintenance.

2. Proposed the simplified method of calculating the reference signatures, which has lower complexity, and free from shortcomings that are inherent in the known theoretical methods for calculating the reference signatures.

3. In order to automate the definition of the reference signatures a new algorithm and simulation program of the signature method diagnosis for digital devices are developed.

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Section 3. Mathematics

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The hypothesis of the Euler-Goldbach and the opposite sieve of eratosthenes

Abstract: The existence of the amount of even number two prime numbers allows us to obtain the sieve of Eratosthenes from very large numbers to decrease. There is a new way to generate primes.

Keywords: hypothesis of the Euler-Goldbach, the sieve of Eratosthenes.

The hypothesis of the Euler-Goldbach (HEG) was established by Euler in 1742 in response to trinary hypothesis Goldbach. Goldbach suggested that every odd number is the sum of three primes (PN). Euler said that if any even number are the sum of two PN (binary hypothesis), trinary hypothesis is confirmed automatically [1; 2]. In 2014 Druzhinin first proved binary option using probability theory [3]. In subsequent works on this subject Druzhinin and Lazarev [4; 5] improved this evidence, in particular, they found the supermom that without theory of probability confirms that every even integer greater than "2" is the sum of two primes. There is the formula for calculation of pairs of such numbers, called the pairs of the Euler-Goldbach (PEG), and obtained good agreement with experiment. These works were handed over to the various specialists in the number theory who are doctors of science and members of the SAR, but still negative feedback or detected mistakes in reasoning Druzhinin is not received.

This article discusses two topics related to theory: the inverse sieve of Eratosthenes and development of the original theory to the case of special groups of PN. The sieve of Eratosthenes, which is more than 2000 years, looks like. Taken a consistent set of natural odd numbers beginning with PN $p_1 = 3$ is considered. All numbers $x_1 = 9 + 6k$, i. e. all numbers are multiples of "3", except for the number "3" are removed. After that the first not deleted number, in this case, $p_2 = 5$, is declared the prime and all other numbers are multiples of "5", $x_2 = 15 + 10k$

are removed. The following not delete number $p_3 = 7$ is the prime, and $x_3 = 21 + 14k$ are removed. Thus, the primes are found sequentially. A characteristic feature of the sieve is that it is not only the first not remote, the number p_m is PN, but the whole segment $\left[p_m, \ p_m^2 - 1 \right]$ contains the new PN that are not uninstalled the previous arithmetic progressions (AP). For example, the interval $[7, 47]$ contains the PN $\{11; 13; 17; 19; 23; 29; 31; 37; 41; 43; 47\}$. This is a direct sieve of Eratosthenes. Reverse the sieve of Eratosthenes, which we offer, consists in the following. Take any even number $M = 2N$, and his left the neighborhood (smaller numbers) is a sieve that selects a large primes.

The logic of action is based on the works of the author [3; 4; 5] and looks like this. **1.** From inequality $p_m \leq \sqrt{M-3}$ basis set fond of HR $A(M,m) = = \{p_1; p_2; \ldots p_m\}$. **2.** From the equality $\left[(N-1)/2 \right] = n$ the period of $B(M,n) = [1; 2; 3; \ldots; n]$ found. Here $[C]$ the greatest integer not exceeding "C". **3.** From a comparison of $M \equiv \mu_k \ (mod \ p_k)$, where $0 \leq \mu_k < p_k$, we find all remainders modulo M in $p_k \in A(M,m)$. **4.** From the comparison $\left[\mu_k + \left((\mu_k + 1)(p_k - 1)/2 \right) \right] \equiv$ $\equiv \beta_k \ (mod \ p_k)$ find the deductions $1 \leq \beta_k \leq p_k$. $\{\beta_k\}$ – is a complete set of minimal positive deductions. **5.** Prepare m AP $y_k = \beta_k + tp_k$ for all the PN of $A(M,m)$. Here $t = \{0; 1; 2; \ldots\}$. **6.** In the interval $B(M,n)$ delete all numbers from the obtained m AP. Remained not deleted numbers z_l give PN $p_l = M - (2z_l + 1)$. It is a consistent

large PN smaller M.

Example. Take $M = 50$.

1. $A(50,2) = \{3;5\}$.

2. $n = [24/2] = 12$. $B = [1,12]$.

3. $\mu_1 = 2$, $\mu_2 = 0$.

4. $[5] \equiv 2(mod\,3), [2] \equiv 2(mod\,5), \beta_1 = \beta_2 = 2$.

5. $y_1 = 2 + 3t$ removes from B the number of $\{2;5;8;11\}$. $y_2 = 2 + 5t$ removes from B the numbers $\{2;7;12\}$. Remain $z = \{1;3;4;6;9;10\}$, which give PN $\{47;43;41;37;31;29\}$. Above we got these numbers from the direct sieve of Eratosthenes.

Communication with the HEG is that obtained great PN partially belong in the PEG, to calculate which use a specified algorithm $[3; 4; 5]$. The practical benefit is to rapidly obtain a large prime. If we plot β_l in ascending order, you can easily find the first not remote z, and thus the prime closed to M. We will show this on the example with $M = 10000$. Here it is necessary to account for the 24 PN of the smaller "100". In ascending order β_l have AP: $\{1 + 13t; 2 + 5t; 3 + 3t; 5 + 7t; 10 + 17t; ...\}$. These AP leave $z = 4$, i.e. $p = 9991$, and $z = 8$, i.e. $p = 9983$.

The second question of this article there is a special PEG. Can an even number $M = 2N + 2$ be the sum of two PN of the form $p = 4s + 1$? In our opinion it can. The sequence is similar to above, but with some differences.

1. We find $A(M,m) = \{p_1; p_2; ... p_m\}$ where $p_m \le \sqrt{M - 5}$.

2. Find the interval $B(M,n) = [1;2;3;...;n]$, where $n = [N/4]$.

3. Generate a set of AP $\overline{x}_k = \alpha_k + t\overline{p}_k$ and $\widehat{x}_k = (\alpha_k + \widehat{p}_k) + t\widehat{p}_k$. Here $\alpha_k = ((d_k - 1)/4)$. d_k is the smallest Prime or a composite number greater than or equal to "5" and a multiple of p_k. PN p_k consist of basic $\widehat{p}_k = 4s + 1$ and the auxiliary $\overline{p}_k \ne 4s + 1$. For example, $\overline{p}_k = \{3; 7; 11; 19; ....\}$, and $\widehat{p}_k = \{5; 13; 17; ...\}$. We are looking for the sum of the number of M from two $\widehat{p}_k$, i.e. $M = \widehat{p}_a + \widehat{p}_b$.

4. Create another group up $y_k = \beta_k + tp_k$ without separating the primes for the main and auxiliary. β_k is found from a comparison of $[((p_k + 1)/2)\mu_k + (\mu_k + 1)\alpha_k] \equiv \beta_k (mod\,p_k)$. $1 \le \beta_k \le p_k, t = 0;1;2;...$

5. From the segment delete numbers all three sequences. The remaining numbers z give special pair of Euler-Goldbach $\{4z + 1; M - 4z - 1\}$.

Example.

$M = 42, N = 21, n = 21/4 = 5, p_{max} \le \sqrt{37}, B(42,5) = [1,5]$, $A(42,2) = \{3;5\}, \alpha_1 = (9 - 1)/4 = 2, \alpha_2 = (5 - 1)/4 = 1$, $\overline{p}_1 = 3, \widehat{p}_2 = 5, \overline{x}_1 = 2 + 3t, \widehat{x}_2 = 6 + 5t, \mu_1 = 0, \mu_2 = 2, [0 + (0 + 1)2] \equiv \beta_1 (mod\,3), \beta_1 = 2, [2 \cdot 3 + (2 + 1) \cdot 1] \equiv \beta_2 (mod\,5), \beta_2 = 4, y_1 = 2 + 3t, y_2 = 4 + 5t$. All preparatory work is done. We remove from the interval $[1,5]$ numbers of these four AP. Deleted AP: $\{2;5\},\{-\},\{2;5\},\{4\}$. Left numbers $z = \{1;3\}$. The number $z = 1$ gives the pair $\{5; 37\}$, number $z = 3$ gives pair $\{13; 29\}$. Illustration this problem is visually. Take all the odd numbers of the form $\gamma = 4s + 1$ from "5" to "47" and place them and $B(42,5)$ according to the matrix rows

$$\begin{pmatrix} 5 & 9 & 13 & 17 & 21 \\ 1 & 2 & 3 & 4 & 5 \\ 37 & 33 & 29 & 25 & 21 \end{pmatrix}$$

The sum of the top and bottom numbers in the columns is equal to the given number $M = 42$. Central line is numbers of columns. You can consider the top row and delete columns with the upper part number of $\{9; 21\}$. After that, the bottom line remains one composite number "25". Remove this column. The first and the third columns giving a PEG are remained. Our method of the work on secondary column with a set AP gives the same result and, moreover, allows to obtain an analytical proof that for $M = 34$ and all numbers of the form $M = 2N + 2$ can be expressed as the sum of two PN from the $p = 4s + 1$. Compute calculations support this conclusion.

Table 1. – Number PEG from M.

Table 1.

M	102	202	302	402	502	602	702	802	902	1002
Number PEG	4	2	3	8	6	13	14	8	4	8

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Modification of the Euler's polygonal curves method as applied to a boundary value problem for a hyperbolic equation

Abstract: Sufficient conditions are obtained that allow to estimate the closeness of the constructed triplet of functions with the help of modification of Euler's polygonal curves method to an exact solution of a semi-periodic boundary value problem for a nonlinear hyperbolic equation with two independent variables.

Keywords: nonlinear hyperbolic equations, semi-periodic boundary value problems, modification of Euler's polygonal curves method, approximate solutions.

In the range $\overline{\Omega} = [0,\omega] \times [0,T]$ the boundary value problem for a nonlinear hyperbolic equation with two independent variables is considered

$$\frac{\partial^2 u}{\partial x \partial t} = f\left(x,t,u,\frac{\partial u}{\partial t},\frac{\partial u}{\partial x}\right), \qquad (1)$$

$$u(x,0) = u(x,T), \quad x \in [0,\omega], \qquad (2)$$

$$u(0,t) = \psi(t), \quad t \in [0,T], \qquad (3)$$

where $f : \overline{\Omega} \times R^3 \to R$, — continuous function, $\psi(t)$ — the function that is continuously differentiable on $[0,T]$ and that fulfills the condition $\psi(0) = \psi(t)$.

Suppose that $C(\overline{\Omega})$ — the space of functions $u : \overline{\Omega} \to R$ that are continuous on $\overline{\Omega}$. For the functions $u(x,t) \in C(\overline{\Omega})$ at the fixed $x \in [0,\omega]$ we introduce the norm $\| u(x,\cdot) \|_1 = \max\limits_{t \in [0,T]} | u(x,t) |$.

The modification of Euler's polygonal curves method as applied to semi-periodic boundary value problems for hyperbolic equations is suggested in the works [1–3]. Sufficient conditions for existence of solution to the problems (1)–(3) were obtained, and the theorems, which establish the values of differences between exact solution and initial approximation, were proven. The result of the report is a further development of modification of Euler's polygonal curves method as applied to the problems (1)–(3). The conditions of solvability of boundary value problems for nonlinear ordinary differential equations and the convergence of a sequence of functions of Euler's polygonal curves method to solution of the problems (1)–(3) were obtained.

The function $u(x,t) \in C(\overline{\Omega})$, which has partial derivatives $\dfrac{\partial u(x,t)}{\partial x}, \dfrac{\partial u(x,t)}{\partial t}, \dfrac{\partial^2 u(x,t)}{\partial x \partial t}$ belonging to $C(\overline{\Omega})$,

is called a classical solution of the problem (1)–(3), if it complies with the equation (1) at all values $(x,t) \in \overline{\Omega}$ and boundary conditions (2), (3).

Let us introduce new unknown functions $v(x,t) = \dfrac{\partial u(x,t)}{\partial x}$, $w(x,t) = \dfrac{\partial u(x,t)}{\partial t}$ and reduce the problem (1)–(3) to the following equivalent problem:

$$\frac{\partial v}{\partial t} = f\left(x,t,u(x,t),w(x,t),v\right), \qquad (4)$$

$$v(x,0) = v(x,T), \quad x \in [0,\omega], \qquad (5)$$

$$u(x,t) = \psi(t) + \int_0^x v(\xi,t)d\xi, \quad w(x,t) =$$

$$= \dot{\psi}(t) + \int_0^x v_t(\xi,t)d\xi \qquad (6)$$

Triplet of the functions $\{u(x,t),w(x,t),v(x,t)\}$ that are continuous on $\overline{\Omega}$ is called a solution of the problem (4)–(6), if the function $v(x,t) \in C(\overline{\Omega})$ has a derivative with respect to t, which is continuous on $\overline{\Omega}$, and complies with the family of periodic boundary value problems (4), (5), where the functions $u(x,t)$, $w(x,t)$ are linked to $v(x,t), \dfrac{\partial v(x,t)}{\partial t}$ functional relations (6).

The problems (1)–(3) and (4)–(6) are equivalent in the sense that, if the triplet $\{u(x,t),w(x,t),v(x,t)\}$ will be a solution to the problem (4)–(6), then the function $u(x,t)$ is a solution to the problem (1)–(3) and, vice versa, if the triplet $\{u(x,t),w(x,t),v(x,t)\}$ is a solution to the problem (4)–(6), then $u^*(x,t)$ will be solution to the problem (1)–(3).

By solving the periodic boundary value problem

$$\frac{dV^{(1)}}{dt} = f\left(0,t,\psi(t),\dot\psi(t),V^{(1)}\right), \qquad (7)$$

$$t \in [0,T], V^{(1)}(0) = V^{(1)}(T)$$

we find the function $V^{(1)}(t)$. By $V^{(1)}(t)$, $\dot V^{(1)}(t)$ we determine the functions:

$$U_0(x,t) = \psi(t) + xV^{(1)}(t), W_0(x,t) =$$

$$= \dot\psi(t) + x\dot V^{(1)}(t), (x,t) \in \overline\Omega$$

By taking the functions that are continuous on $[0,\omega]$ $\rho_1(x)$, $\rho_2(x)$ we form the sets

$$G_0 = \left\{(x,t,u,w,v) : (x,t) \in \overline\Omega, |u - U_0(x,t)| < \rho_2(x), \right.$$

$$\left. |w - W_0(x,t)| < \rho_2(x), |v - V^{(1)}(t)| < \rho_1(x)\right\},$$

$$S(U_0(x,t),\rho_2(x)) = \left\{u(x,t) \in \overline\Omega : \|u - U_0(x,\cdot)\|_1 < \rho_2(x)\right\},$$

$$S(W_0(x,t),\rho_2(x)) = \left\{w(x,t) \in \overline\Omega : \|w - W_0(x,\cdot)\|_1 < \rho_2(x)\right\},$$

$$S(V^{(1)}(t),\rho_2(x)) = \left\{v(x,t) \in \overline\Omega : \|v - V^{(1)}(\cdot)\|_1 < \rho_1(x)\right\},$$

Conditions A. Suppose that the boundary value problem (7) has a solution $V^{(1)}(t)$; there are functions $\rho_1(x) > 0$, $\rho_2(x) > 0$ that are continuous on $[0,\omega]$; the function $f(x,t,u,w,v)$ in the set G_0 has uniformly continuous partial derivatives with respect to u,w,v; and the following inequations are correct:

$$|f_u(x,t,u,w,v)| \le L_1(x), \ |f_w(x,t,u,w,v)| \le L_2(x),$$

$$|f_v(x,t,u,w,v)| \le L_3(x) \qquad ,$$

where $L_i(x)$, – the functions that are continuous on $[0,\omega]$, $i = 1,2,3$.

To find solution to the problem (4)–(6) we use modification of Euler's polygonal curves method. The interval $[0,\omega]$ is divided in increments of $h > 0$ into m parts: $mh = \omega$ and with every increment we solve periodic boundary value problems for ordinary differential equations.

Determine the functions through equations:
$v^{(0)}(t) = 0, \dot v^{(0)}(t) = 0, u^{(0)}(t) = \psi(t),$
$w^{(0)}(t) = \dot\psi(t), t \in [0,T]$
and by solving periodic boundary value problem
$\frac{dv^{(1)}}{dt} = f\left(0,t,\psi(t),\dot\psi(t),v^{(1)}\right), t \in [0,T], v^{(1)}(0) = v^{(1)}(T),$
we find the function $v^{(1)}(t)$. By $v^{(1)}(t)$, $\dot v^{(1)}(t)$ we determine the functions:
$u^{(1)}(t) = \psi(t) + hv^{(1)}(t), w^{(1)}(t) = \dot\psi(t) + h\dot v^{(1)}(t), t \in [0,T].$

Find the function $v^{(2)}(t)$ by solving periodic boundary value problem $\frac{dv^{(2)}}{dt} = f\left(h,t,u^{(1)}(t),w^{(1)}(t),v^{(2)}\right),$
$t \in [0,T], v^{(2)}(0) = v^{(2)}(T)$.

By $v^{(1)}(t)$, $\dot v^{(1)}(t)$ and $v^{(2)}(t)$, $\dot v^{(2)}(t)$ we determine the functions:

$$u^{(2)}(t) = \psi(t) + h[v^{(1)}(t) + v^{(2)}(t)],$$

$$w^{(2)}(t) = \dot\psi(t) + h[\dot v^{(1)}(t) + \dot v^{(2)}(t)], \ t \in [0,T]$$

Supposing that $u^{(i)}(t), w^{(i)}(t), v^{(i)}(t)$ are known, we find the function $v^{(i+1)}(t)$ by solving the boundary value problem

$$\frac{dv^{(i+1)}}{dt} = f\left(ih,t,u^{(i)}(t),w^{(i)}(t),v^{(i+1)}\right), t \in [0,T], \qquad (8)$$

$$v^{(i+1)}(0) = v^{(i+1)}(T), i = \overline{1,m}.$$

Define the functions $u^{(i+1)}(t), w^{(i+1)}(t)$ in $v^{(i+1)}(t), \dot v^{(i+1)}(t)$ through the following equations

$$u^{(i+1)}(t) = \psi(t) + h\sum_{j=0}^{i+1} v^{(j)}(t),$$

$$w^{(j)}(t) = \dot\psi(t) + h\sum_{j=0}^{i+1} v^{(j)}(t),$$

$$t \in [0,T], \ i = \overline{1,m}.$$

Let us consider the system of periodic boundary value problems for ordinary differential equations.

$$\frac{dv^{(i+1)}}{dt} = f\left(\begin{matrix} ih,t,\psi(t) + h\sum_{j=0}^{i+1} v^{(j)}(t),\dot\psi(t) + \\ + h\sum_{j=0}^{i+1} \dot v^{(j)}(t), v^{(i+1)} \end{matrix}\right), \qquad (9)$$

$$v^{(i+1)}(0) = v^{(i+1)}(T), \ t \in [0,T], \ i = \overline{1,m} \qquad (10)$$

On $\overline\Omega$ we construct the functions

$$U_h(x,t) = \psi(t) + h\sum_{j=0}^{i+1} v^{(j)}(t) + v^{(i)}(t)(x - (i-1)h),$$

$$x \in [(i-1)h,ih),$$

$$W_h(x,t) = \dot\psi(t) + h\sum_{j=0}^{i+1} v^{(j)}(t) + \dot v^{(i)}(t)(x - (i-1)h),$$

$$x \in [(i-1)h,ih),$$

$$V_h(x,t) = v^{(i+1)}(t)\frac{x - (i-1)h}{h} + v^{(i)}(t)\frac{ih - x}{h},$$

$$x \in [(i-1)h,ih).$$

Theorem. Let the condition A be fulfilled and the following inequations take place:

1) $\left|\int_0^T f_v(x,t,u,w,v)dt\right| \ge \delta > 0$; for all $(x,t,u,w,v) \in G_0$;

2) $\left(B + Ah\Delta^{(1)}\right)\left(1 + Ah\right)^{\frac{\omega}{h}} + d_h(x) +$

$+ B_h(x)\exp\left(\int_0^x c_h(\gamma,\xi)d\xi\right) < \rho_1(x),$

3) $\left(B + Ah\Delta^{(1)}\right)\left(1 + Ah\right)^{\frac{\omega}{h}} +$

$+ B_h(x)\exp\left(\int_0^x c_h(\gamma,\xi)d\xi\right) < \rho_2(x).$

Then: a) the problem (1)–(3) in $S(U_0(x,t),\rho_2(x))$ has unique solution $u^*(x,t)$,

b) for any $m = 1,2,3,\ldots \left(h = \dfrac{\omega}{m}\right)$ the problem (9),

(10) has unique solution $\{v^{(1)}(t),...,v^{(m+1)}(t)\}$, where $\{v^{(k)}(t)\} \in S(V^{(1)}(t), \rho_2((k-1)h)), k=1,2,...,m+1$, and the valuation functions are correct

$$\max\left(\left\|u^*(x,\cdot)-U_h(x,\cdot)\right\|_1, \left\|\frac{\partial u^*(x,\cdot)}{\partial t}-W_h(x,\cdot)\right\|_1\right) \leq \quad (11)$$

$$\leq B_h(x)\exp\left(\int_0^x c_h(\gamma,\xi)d\xi\right),$$

$$\left\|\frac{\partial u^*(x,\cdot)}{\partial x}-V_h(x,\cdot)\right\|_1 \leq d_h(x)+$$

$$(12),$$

$$+c_h(\gamma,x)B_h(x)\exp\left(\int_0^x c_h(\gamma,\xi)d\xi\right),$$

where the functions $A, B, d_h(x), B_h(x), c_h(\gamma,x), \Delta^{(1)}$ are determined by the initial data of the problem (1)- (3), and at $h \to 0$ the functions $d_h(x), B_h(x)$ tend towards zero uniformly in $x \in [0,\omega]$. The valuation functions (11), (12) at $h \to 0$ provide the convergence of modification of Euler's polygonal curves method to the solution $-u^*(x,t)$ of the problem (1)–(3) and its partial derivatives $\frac{\partial u^*(x,\cdot)}{\partial t}, \frac{\partial u^*(x,\cdot)}{\partial x}$.

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Section 4. Machinery construction

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Quality assessment of the regulation of hydraulic system of wheel vehicle in terms of stability and oscillation of the system

Abstract: The article deals with the problem of assessing the quality of the regulation of hydraulic system of a wheel vehicle. The limits of stability region are determined according to the indicators of the degree of stability and oscillation of the system.

Keywords: guidance, hydraulic system, regulation, oscillation, stability, wheel vehicle, object, model.

Due to excitation effects on the regulation or control system, the operating mode of the system is broken at some points in time. When a given state is restored, some transient processes occur in the system, accompanied by a change in regulated quantities in time. The main requirement that the regulation system must satisfy is to provide the mode specified for the regulated facility. However, due to the discrepancy between the characteristics of the regulator and the regulated object, the requirements for the system may not be met. There are cases when the system is unstable. In such systems, after accidental excitation, the undamped oscillations or the oscillations with increasing amplitude in time arise; or the deviation of regulated quantity increases monotonically in time [1].

Consider the system [2]

$$m\ddot{x} + \mu\dot{x} + cx = \beta \qquad (1)$$

where $\mu = F_u^2 R_0$, m — is a mass of the plunger of hydraulic system, K - a magnification coefficient, F_u — a

working area, equal to plunger area, c — a spring stiffness, R_0 — hydraulic resistance.

Dividing all coefficients of equation (1) by c, it is reduced to its standard form

$$T_2^2 \frac{d^2x}{dt^2} + T_1 \frac{dx}{dt} + x = K \qquad (2)$$

where $T_2 = \sqrt{\dfrac{m}{c}}$, $T_1 = \dfrac{F_u^2 R_0}{c}$, $K = \dfrac{\beta}{c}$.

Coefficients T_2 and T_1 entering equation (2) are constants, coefficient K is a transmission coefficients. In equation (2) taking x_0 and β_0 as basic quantities, the following dimensionless variables are introduced

$$\bar{x} = x/x_0, \qquad \bar{\beta} = \beta/\beta_0 \qquad (3)$$

Substituting in equation (2) with relationship (3) the variables x_0 and β for $\bar{x}$ *and* $\bar{\beta}$, we get

$$T_2^2 \frac{d^2\bar{x}}{dt^2} + T_1 \frac{d\bar{x}}{dt} + \bar{x} = K_0\bar{\beta} \qquad (4)$$

where $K_0 = \dfrac{\beta_0}{c}$.

Differential equation (4) may be represented as

$$\frac{dx_1}{dt} = x_2,$$

$$\frac{dx_2}{dt} = -\frac{1}{T_2^2} x_1 - \frac{T_1}{T_2^2} x_2 + \frac{K_0}{T_2^2} U \qquad (5)$$

and by relationship

$$\bar{x} = x \qquad (6)$$

where $U = \beta$.

Knowing the values of the variables x_1 and x_2 at time t_0 and the input action of U for all $t > t_0$, the state of the system may be determined at any time $t > t_0$ and the response of the system $\bar{x}(t)$ may be found.

We will assess the quality of regulation in terms of stability and oscillation.

The type of transient process under given law of influence on the system depends on the denominator and the numerator of transfer function of the system. The transfer function of system (4) in Laplace images has the form $[3]$

$$W(x) = \frac{K_0}{T_2^2 s^2 + T_1 s + 1}. \qquad (7)$$

Introduce the designations into relation (7),

$$T_2 = T \text{ and } \psi = \frac{T_1}{2T}, \qquad (8)$$

where ψ – is a coefficient of relative damping. Substituting expression (8) in (7), we get

$$W(s) = \frac{K_0}{T^2 s^2 + 2\psi T s + 1}. \qquad (9)$$

At $s = j\omega$ transfer function (9) becomes amplitude – phase frequency characteristic $(APFC)$ of the system (5).

$$W(j\omega) = \frac{K_0}{1 - \omega^2 T^2 + j\omega 2\psi T}. \qquad (10)$$

Real $p(\omega)$ and imaginary $q(\omega)$ frequency characteristics are obtained by multiplying the denominator and the numerator of APFC (10) by complex expression, conjugated with the denominator. As a result we get

$$p(\omega) = \frac{K_0(1 - \omega^2 T)}{(1 - \omega^2 T^2)^2 + (2\psi\omega T)^2}$$

$$q(\omega) = -\frac{2K_0\psi\omega T)}{(1 - \omega^2 T^2)^2 + (2\psi\omega T)^2} \qquad (11)$$

For the values of ω, located within the range from 0 to $+\infty$, amplitude – phase frequency characteristics are shown in Fig. 1 by solid lines, and for negative values of ω — by dotted lines, for the system with the following parameters:

$$m = 160, \quad k_0 = 1{,}06, \quad c = 1{,}125,$$

$$\beta = 1, \quad \beta_0 = 1, \quad x_0 = 0{,}2 \, mm.$$
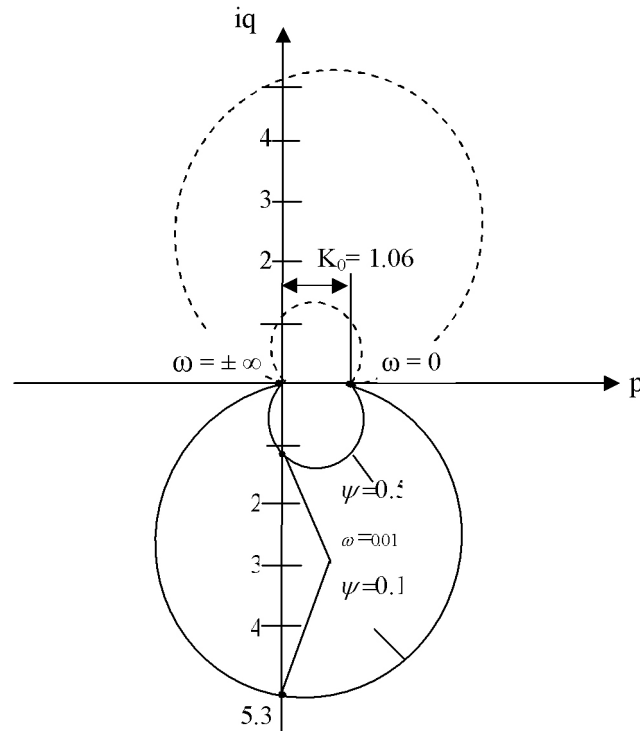
Figure 1.

If the numerator of transfer system is equal to constant value — to magnification coefficient K of the system, then the quality assessment of the regulation is conducted according to the location of the roots of characteristic equation

$$D(\lambda) = a_2\lambda^2 + a_1\lambda + a_0 = 0 \qquad (12)$$

on complex plane.

The boundaries of the region in which the roots λ_i of characteristic equation (12) are located on complex plane are determined by three indicators $[3]$ (Fig. 2):

a) by the degree of stability or minimal removal of the root from linear axis $\eta = \left| \operatorname{Re} \lambda_i \right| \min$;

b) by maximum removal of the root from imaginary axis $\xi = \left| \operatorname{Re} \lambda_k \right| \max$;

c) by oscillation $\mu_* = \left| \operatorname{tg} \gamma_l \right|$.

Figure 2.

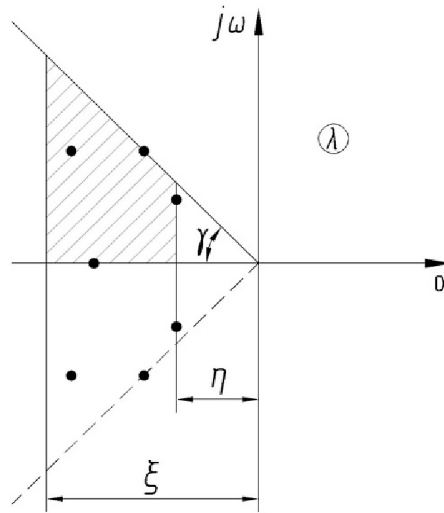If the system is stable, then the roots of characteristic equation must lie to the left of imaginary axis, and are represented in the form

$$\lambda_i = -\alpha_i + j\omega_i, \qquad (13)$$

where $\alpha_i > 0$.

With relationship (13) the oscillation is

$$\mu_* = \left(\omega_i / \alpha_i \right) \max. \qquad (14)$$

For the discussed case according to equation (12)

$$\eta = \frac{T_1}{2T_2^2}, \quad \mu_* = \pm \frac{\sqrt{T_1^2 - 4T_2^3}}{T_1}. \qquad (15)$$

The degree of stability characterizes the rapidity of the end of transfer processes in the system: the greater η, the faster the regulated quantity reaches a steady-state value with a specified accuracy.

To evaluate the quality of regulation by the degree of stability, we introduce into characteristic equation (12)

$$\lambda = Z - \eta. \qquad (16)$$

Obtained equation

$$c_2 Z^2 + c_1 Z + c_0 = 0, \qquad (17)$$

is called a biased equation; the coefficients of biased equation are the functions of the degree of stability and coefficients of initial equation.

If, for the stability of the system it is enough that the coefficients are $a_2 > 0$, $a_1 > 0$, $a_0 > 0$, then to ensure a specified degree of stability η, it is necessary for the coefficients of biased equation (17) to be positive. These coefficients are determined by introducing into equation (12) the value of λ; according to relationship (16), we get

$$c_2 = a_2, \quad c_1 = a_1 - 2a_2\eta \quad c_0 = a_2\eta^2 - a_1\eta + a_0. \quad (18)$$

Meeting the terms of stability $c_2 > 0$, $c_1 > 0$, $c_0 > 0$ for biased equation (16) ensures the degree of stability

η of the initial system. In addition, the coefficients of equation (12) must be positive and satisfy the inequalities $a_2 > 0$, $a_1 > 2a_2\eta$, $a_2\eta + a_0 >_1 \eta$. The oscillation shows how far the system is away from the stability boundary.

The exponent of subsidence ratio ψ is defined as follows:

the component of transient process, which for the case under consideration has the form

$$X_i(t) = C_i e^{-\alpha_i t} \sin(\omega_i t + \phi_i), \qquad (19)$$

takes place in the presence of complex roots of characteristic equation (12). After one period $T = \dfrac{2\pi}{\omega_i}$, the amplitude is

$$A_i = C_i e^{-\alpha_i t},$$

the component $X_i(t)$ of transient process will decrease to

$$A_{iT} = C_i e^{-\alpha_i\left(t + \frac{2\pi}{\omega_i}\right)} = A_i e^{-2\pi\frac{\alpha_i}{\omega_i}}, \qquad (20)$$

the attenuation over a period is determined by relationship

$$\psi_T = \frac{A_i - A_{iT}}{A_i} = 1 - \frac{A_{iT}}{A_i}.$$

With relations (14) and (20), we determine

$$\psi_T = 1 - e^{-\frac{2\pi}{\mu_*}},$$

or

$$\mu_* = \frac{2\pi}{\ln \dfrac{1}{1 - \psi_T}}. \qquad (21)$$

Thus, the less the oscillation μ_*, the greater the attenuation ψ_T over the period and the margin of stability.

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Section 5. Mechanics

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Oil displacement by water in an electric field

Abstract: The paper deals with the efficiency of the electric field effect on oil recovery process. Also shows the possibility of electro-osmotic effects on oil displacement by water.

Keywords: condition, water, electric, electrolyte.

The current stage of development of the oil industry in Kazakhstan is characterized by complicated conditions of field development, increased share of hard and decreased the proportion of active oil reserves, a sharp increase in water cut, the deterioration of the technical condition of wells, etc.

In general, the conditions for fields that are in late stage development, alternative constraint falling oil production and increase oil leak may be the impact on hard-and residual oil through increased use of complex geological and technical measures, modern methods of enhanced oil recovery and processing of bottom zones of wells.

During the last decade there is a continuous deterioration of the quality status of the raw material base of the oil industry due to the significant development of reserves of highly productive fields that are in continuous operation. A significant part of the oil fields in Western Kazakhstan is in the late stages of development, which is characterized by a constant decline in oil production, while increasing its water content.

Improving the efficiency of extraction of hydrocarbons from subsurface largely depends on the creation of new process control near the wellbore. Bottom hole zone, this area belonging to both the reservoir and the well itself. It not only focus but also enhanced many complications that accompany the process of extracting hydrocarbons from oil and gas reservoirs. Their diversity and complexity caused the appearance of a significant number of different techniques and technologies intensification of oil.

Despite the theoretical bases of many different methods to increase well productivity impact on bottom zone and technology of their conduct, yet the success of many methods remains low at 40–60%. This is due to the fact that the methods used have some disadvantages: the awkwardness of technology; insufficiently developed theoretical principles of design processes; insufficiently informed choices wells for various methods of influence and their priority; insufficient account of the properties and structure of a particular well bottom zone.

At present, for various reasons in Western Kazakhstan idle large number of wells. For enhanced oil and gas recovery oil gas increase at different stages of development of hydrocarbon deposits are widely used for more than 70 different efficiency technologies and methods of action.

Thus, injection of large amounts of water leads to the precipitation of inorganic salts in the formation and the well

bore itself zone. Application of acidizing, the use of surface-active agents (surfactants), particularly hydrocarbons or organic additives or their products, environmentally safe and leads to the destruction of oilfield equipment. The use of thermal methods, and particularly in-situ burning, accompanied by increased destruction of productive reservoirs and sand production, increasing aggressiveness produced products due to combustion products, education in the formation of persistent oil-water emulsions, etc.

Quite effective was the use of hydraulic fracturing (HF) to create additional channels deep in the reservoir. Through this action changes the characteristics of not only effective drainage area, but also the formation itself; at the expense of neighboring wells intensify its operation. However fracturing technology is costly, complex technological equipment, and under the influence in areas near the oil-water contact (OWC), often as a result of hydraulic fracturing of oil instead of receiving water.

Studies show that one of the effective methods of intensification of oil may be the electrical action on the producing formation.

In issue [1] describes the use of an additional factor contributing to the movement of water in the reservoir effect of the electric field at the bottom of the well.

The electric field can change the configuration of the hydrodynamic field, which in essence is the basis of the electroosmotic effects and the filtering process.

Detailed theory of electro, considered in issue [2; 3] It should be noted that electroosmotic is widely used in hydraulic industry when grouting.

In 1936 at the First International Conference on Soil Mechanics L. Kazagrande, proposed a method of processing clay soils DC whereby the bearing capacity of soils is increased five to ten times. In this method the liquid through a clay soil texture (moisture content 80%) is passed direct current voltage of 300–500V and 8–14A, as long as the soil does not solidify.

The successful use of the method of work contributed to Casagrande K. Endelya and E. Gofman [5]. They confirmed the improvement of the physical and mechanical properties of the clay after treatment with direct current.

More research to improve the properties of clay soils under the influence of DC were conducted laboratory drilling oil and gas wells Oil Institute of the USSR Academy [6]. These studies showed that the determining factor in consolidating the clay when exposed to an electric current, is the exchange reaction between the caution uptake.

Electricity costs are determined by the specific conductivity of soil near and depend on the location of the electrodes. In the wild, according to research per-

formance pumping units increased to 0.16 m/kWh. To release water from the soil moisture capacity 10%, conductivity $\gamma = 4,5 - 10 - 1$ 1/ohm-cm and the coefficient $k^2 = 0.1m/0.9$ kWh required to 1m.

The effectiveness of the electric field is determined by the coefficient K has the dimension of m/a, i.e, determining how many meters of piezometric head unit corresponds to the applied voltage. In the case of complete coincidence of the boundary surfaces of the electric and hydrodynamic field configuration and the latter does not change the impact of the electric field is equivalent to the change in the value of piezometric head.

The greatest effect is to increase the intake capacity is achieved using electro-osmosis. In issue [7], the authors investigated the possibility of electroosmotic effect on the displacement of oil by water.

In all cases, the use of electroosmotic effects led to the isolation of additional quantities of oil sample, leading obviously to reduce residual oil saturation. Improved recovery are within a few percent of the original oil content. However, the authors found themselves out of work in the influence of salt water on the displacing oil recovery, which was noted in their findings.

If a solid electrolyte is to make the electrodes conductive and the voltage feed to them, the electrolyte ions are set in motion, and an electric current. Positively charged ions (cations) move towards the negative electrode (cathode), negative ions (anions) move to the positive electrode (anode). Reaching the corresponding electrode, ions give him redundant or obtain the missing electrons and become neutral atoms or molecules.

Mineralized water as the electrolyte is moved by the difference potential, moreover, under the influence of the field E. current is dehydrated clay minerals also leads to increased permeability to water and oil.

A significant role in the movement of saline water also plays a so-called double force, which is formed on the surface of minerals concentrating negative charges. In a double-layer two different interlayer: one fixed at the mineral surface and the second movable.

The interaction between these layers is expressed as in-building. If you have any e-field occurs brine electroosmotic flow in the movable sublayer.

Additional water consumption due to electroosmotic effects in the persistent form of the electric and hydrodynamic field is proportional to the electric current, and also depends on the relative positions of sources of inflow and electrodes.

Depending on the chemical nature of the electrolyte and the electrodes, ions are neutralized or stand on the

electrodes, or react with the electrodes or diluent. The chemical reactions that take neutralize ions form a secondary reaction. Products of secondary reactions at the electrodes are allocated or go into solution.

Thus, the current flow through the electrolyte to the electrodes accompanied by the release components electrolyte electrode system – a typical electrolyte occurs acid-reduction reaction. Occurs at the cathode recovery process -Transfer electron action from the solution, and the anode oxidation process occurs – electron anions returns. Therefore, the cathode is the reducing agent, anode-oxidant.

As is well known, mineralized water oil fields are typical electrolytes – aqueous solutions of salts and composition are calcium chloride, magnesium chloride, and hydrocarbonatrium water.

Oil, consisting mainly of a mixture of various hydrocarbons, is a dielectric. However, some oil formation conductivity different from the conductivity of the same oil to the surface. In situ oil is in equilibrium with the buried water, partially saturated with moisture and gas.

Oil-water-gas in the pores are in dynamic equilibrium. Because of the large oil resistance, can not be electrolyzed.

When electro processing layers converts electrical energy into heat, which is accompanied by changes in temperature, evaporation and condensation, chemical reactions (electrolysis), electro osmosis, electrophoresis and mechanical deformations of the rock matrix.

When electro processing formation around the current conductor, a magnetic field acting on the charged particles, and exerts a force on adjacent current-carrying conductors.

Liquid particles that are in the low-permeability interlayers will experience than the pressure forces the action of electric and magnetic forces. The electric current excites the magnetic field, ie, has a magnetizing force is numerically equal to the most current.

The magnetic field acts on the magnetic substance dissolved in a liquid and a solid dielectric; last magnetizing reinforce the magnetic field. Especially enhanced field, when the ferromagnetic material and contains cause additional mechanical strength.

Thus, arising electroprocessing seams magnetic and electric forces can effectively drain the reservoir heterogeneity and remove residual oil from non-performing layers.

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Wave device for near wellbore zone treatment

Abstract: Near wellbore zone treatment using pressure impulse creating device is considered. Proposed a new high frequency wave creating devicethat provides the possibility of strengtheningcreated pressure impulses.

Thus, as it becomes obvious, adding the jet-pump to the construction of the device and aligning its useful work together with other constructive elements leads to the increasing frequency and strengthening of the waves created by the device because extra part of the borehole liquid directed to the device through the jet-pump.

Keywords: layer, device, wave, jet-pump, hydrodynamic radiator, nozzle, diffuser, check valve, throttle, frequency.

Introduction. In the oil industry waves are used widely for treatment of reservoir. The spread of waves in the porous media and its impact on filtration of oil and gas allow achieve many positive results. Existing developed technologies in this area based oncreating disperse liquid systems using theoretical and experimental investigations conducted in the laboratories and injecting these systems into the near wellbore zone of reservoirs using special devices. Along with the developed technologies in this area a number of devices able to create oscillation and vibrating waves have been created for implementing these technological operations [1–3]. But it is necessary to note that the majority of the waves creating devices are able to create low frequency waves and their ability to create high frequency waves is rather limited. It reduces their efficiency and results in their limited practical application [1–3].

It is well known that the wave emerged from periodical forcing function gradually covers the whole system and after some time oscillating waves with stable amplitude are established. Wave spread in porous media, besides the rock and liquid physical properties also depends on interaction of the hard and liquid phases [1]. When the low frequency waves begin to spread in the porous media, the vibrations of the wave and rock skeleton become co-phased.With the increase of the frequency the spread of the wave in the liquid phase lags behind its spread in the rock as a result of the inertial and viscous forces.

The researches evidence [1] that the increase in the frequency of waves and of their amplitude in some cases have a positive impact on pushing the oil from the pore and on washing the collimated particles.

However, there is a great need for the development and implementation of new technologies and new devices based on improved mechanism of acoustic wave's impact on the technological processes.

Statement of the problem. As it was noted above, in many casesphysical field creating devices are widely used in the oil industry for increasing the efficiency of theworks conducted forregulating the key performance indicator ofthe reservoirs and wells and for increasing their productivity. Such devices may include vibrators for near wellbore zonetreatment [4], devices for wells startup (flow initiation) [5], devices for perforation

[6], devices for the near wellbore treatment and washing [7].

Disadvantages of these devices are their capability to create only waves of limited frequency (up to 500 Hz), low reliability because of the moving mechanical parts, weak parameter of produced waves due to non-synchronic work of the some main devices and low efficiency of work because of the said.

Therefore, there is a need inovercoming above-mentioned disadvantages, developing more effective oscillating wave devices and applying them appropriately to the production processes. Taking all this into account, a new type of wave device is proposed.

The goal in the development of the device is to increase the efficiency of the device by increasing liquid rate which passes through the hydrodynamic radiator (wave generator) achieved byaligning the work of the hydro-dynamic radiator (wave generator) and the jet-pump.

The set forth goal is achieveddue to proposed new near wellbore zone treatment and well start up device consisting of the jet pump which inlet connected with tubing, hydro-dynamic radiator (wave generator) located below jet pump and transmitting pipes connecting space under the packer and annulus with jet pump and with hydro-dynamic radiator (wave generator). Jet pump's diffuser outlet connected with inlet of hydro-dynamic radiator (wave generator) and with the annulus. The throttle is installed at the outlet of transmitting pipe to the annulus and the check valve is installed at the entry of transmitting pipe from space under the packer into the reception camera of jet pump.

The main point in the work of the device may be described like this: during the near wellbore zone treatment the liquid sucked by the jet-pump from the annulus is added to the liquid pumped to the pipes from the surface, it passes through the hydro-dynamic radiator (wave generator) and as a result it strengthens created waves (but in the existing devices the liquid only from the surface passes through the hydro-dynamic radiator). Installation of a throttle at the exit of transmitting pipe into the annulus is aimed at regulating the work of the hydro-dynamic radiator (wave generator) during the well start up and reducing the pressure in the annulus.

The scheme of the proposed device is given below (Fig. 1). The device consists of the following parts: a jet-pump 2 connected to the tubing 1, its inlet nozzle 3, mixing 4 and reception 5 cameras, diffuser 6, its outlet 7, hydro-dynamic radiator (wave generator) 8, its tangential inlet 9, the canal 10 which connects the outlet 7 of diffuser 6 with the inlet 9 of hydro-dynamic radiator (wave generator) 8, transmitting pipes 13,14 connecting the outlet of the canal 10 with the annulus 11 and with the space under the packer 12, the check valve 15 installed on transmitting pipe 13 at the inlet of the reception camera 5 of the jet-pump and the throttle 16 installed at the outlet of transmitting pipe 14 into the annulus.

The wave device is lowered into the borehole with tubing and allows begin the operation in two cases:

when the absorption ability of the layer is sufficiently enough.

The device operates as it is described below:

When the absorption ability of the treated layer is sufficiently enough, the outlet of the annulus to the surface is closed at the wellhead. To begin the operation the reagent for the treatment is pumped into the layer through the tubing 1, jet-pump and when it is limited.

2, canal 10 and hydro-dynamic radiator (wave generator) 8. When the reagent passes through the inlet nozzle 3 of the jet pipe 2 and through the reception camera 5 and enters the mixing camera 4, then through the transmitting pipe 13 the liquid is sucked from under packer space 12, passes through the tubing 1 and mixes with the liquid which enters the mixing camera 4 through the nozzle 3.
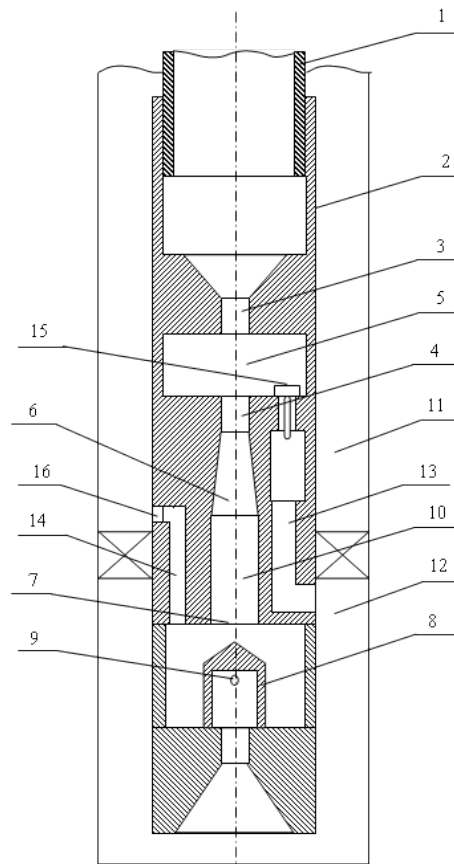

Figure 1. Device for the treatment of reservoir's near wellbore zone. 1-Tubing; 2-Jet-pump; 3-Inlet nozzle; 4-Mixing camera; 5-Reception camera;6-Diffusor; 7-Diffusor outlet;8-Hydro-dynamic radiator (wave generator); 9-Tangential inlet of generator (radiator); 10-Canal which connects the diffusor with the annulus and with the generator (radiator); 11-annulus; 12-Underpacker space; 13, 14-Transmitting pipes; 15-Chech valve; 16-Throttle element

The volume of liquid passed from diffuser 6, canal 10 and hydrodynamic radiator (wave generator) 8, is the total of the liquid volume pumped from the surface through the tubing 1 and through the nozzle 3 and the liquid volume sucked from underpacker space 12 through the transmitting pipe 13, and it will increase the power of

the wave. In this case, for comparison, the power of the wave created by the existing devices will be based only on water pumped through the pipeline 1, because this time the jet-pump will not work.

When the absorption capacity of the borehole is limited, the outlet of the annulus at the wellhead is opened,

liquid pumped through the tubing 1 passes through the jet-pipe2, entersinto annulus11 through the transmitting pipe 13 and throttle element 16, a part of this liquid will be directed to the surface, the rest will mix with the liquid by passing through the tubing 1, enter through the nozzle 3 to the mixing camera 4 and together again will be transmitted to under packer space 12 by passing through hydrodynamic radiator (wave generator). In this case again the volume of the liquid, which passes through the hydrodynamic radiator, will be equal to the total of the working liquid pumped from the surface and the liquid sucked from the under packer space. In the known existing devices all the liquid sucked by the jet-pump from the under packer space is transmitted through the annulus to the surface, so less liquidvolume passes through the generator.

Thus, as it becomes obvious, adding the jet-pump to the construction of the device and aligning its useful work together with other constructive elements leads to the increasing frequency and strengthening of the waves created by the device because extra part of the borehole liquid directed to the device through the jet-pump.

Experimental researches results. To determine the impact of the added jet-pump to the device, special stand experiments have been conducted in laboratory conditions. The tests have been conducted by determining the hydraulic resistance in both cases, that is, when the device was put into operation with the addition of the jet-pump and without it. For this purpose at different rate of water pumped with the washing unit pressure loss has been measured by precise manometers. The results of the stand tests have been shown in Fig. 2:
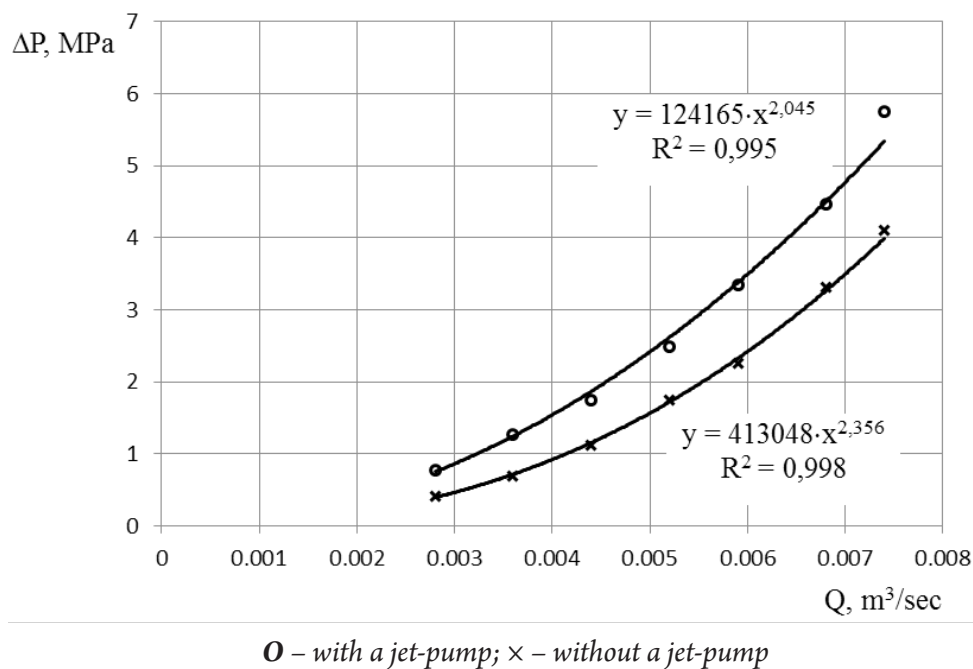

O – with a jet-pump; × – without a jet-pump
Figure 2. Pressure loss vs. liquid rate with and without working jet-pump

As it is seen from Fig.2, when the jet-pump is at work, the power of the device and the frequency of generated waves grow significantly.

The experimental dependences shown in Fig.2 may be described by the following equations:

$$\Delta P_1 = 124165 \cdot Q^{2.045} \qquad (1)$$
$$\Delta P_2 = 413048 \cdot Q^6 \qquad (2)$$

Here ΔP_1 and ΔP_2 – pressure loss with and without working jet-pump correspondingly, MPa, Q – liquid rate which has passed through the device, in cubic meter per second.

In both cases evaluating pressure loss is possible by dividing equation (1) to equation (2):

$$\Delta P_1/\Delta P_2 = 0.3 \cdot Q^{-0.311} \qquad (3)$$

The calculations using equation (3) show that according to the conducted experiments pressure loss varies within 27–47%.

Thus, the application of the proposed device in all the cases allow create intensive pressure waves during the near wellbore zone treatment.

Results: For near wellbore zone treatment new pressure impulse creating device has been proposed and described its advantages in comparison with the existing ones.

The stand tests of the device showed that the rise of pressure loss in the jet-pump and hydrodynamic radiatorwhich are the main parts of the device and the growth of liquid rate that passes through the device, power and frequency of the pressure waves sufficiently increase.

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Section 6. Chemistry

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Obtaining and application of rubber mixtures based on isoprene (sri-3) and functional group polymers

Abstract: Various compositions have been obtained on the basis of polymer mixtures and their physic-chemical properties heat and ozone durability, cords and dynamic characteristics of bond strength with metals have been learned. Influence of various groups on compositions properties has been clarified.

Keywords: ethylene, propylene, composition, high molecular composition, chemical modification, mechanico-chemical modification, modification of polymers during treatment.

As a result of investigations influence of various factors on the interaction of rubbers with functional group polymers has been studied. It has been shown that interaction between rubber and functional group polymers is more effective at 120–180 °C temperature interval. This efficiency has been studied by the change of viscosity and it has been shown that various functional group polymers influence on effective viscosity change of EAS.

It has been determined that physico-mechanical properties of vulcanizates of compositions having high effective viscosity are higher.

Practical significance of the carried out investigation is that on the basis of heat durable EAS and other rubbers-butadiene styrol (BSR), isoprene (SRI-3), butyl rubber (BR) mixtures, rubber mixtures (compositions) be used in modern synthesis industry have been obtained.

Carreed out investigations showed that at present suggested compositions are used in the industry. Rubber mixtures in comparison with SRI-3 and butadiene styrol rubbers have the properties more resistant to heat, aging and durable to multi deformation, tear.

Modification of high molecule compounds with various methods is one of the main directions in purposeful change of known polymer materials properties [1–3]. It is connected with that industrial or small volume production of polymers having new property is connected with the solution of ecological and practical problems. As a result of study of physics and chemistry of polymer mixtures it is possible to obtain compositions with high physico-mechanical property on the basis of functioanal group polymers [4–9].

1. SREPT-60, SREPT-40-ethylene-propylene. Third monomer-dithiclopentadien;% mass 2,5–3.

Unsaturation,% mol – 1,5–1,9

Viscosity according to Muni-40 and 60

2. SRI-isoprene rubber;

3. KP-50 chloroprene rubber;

4. BK-2045 T-butyl rubber

Unsaturation,% mol-2,0 ± 0,2

Viscosity according to Muni-45 and 55

5. PVC-E6250]-polyvinylchloride

Chtorine quantity, % mass 62 ÷ 65

6. CAPP-chlorated atactic polypropylene chlorine quantity, % mass 50,7

Decomposition keeping temperature, °C – 142

7. SCAPP-sulphachlorated atactic polypropylene (synthesized in the laboratory)

Chlorine quantity, % mass-35

Sulphur quantity, % mass-0,75

Molecule mass-1400

Following plasticifators have been used in the composition preparing:

DBF-Dibutylftalat

MQF-9-oligoetheracrelate

Sulfanol;

Density, g/sm^3 – 0,870

Quantity of active substances,% – 47.5

Quantity of chlorine in the mixture of functional group polymers and other rubbers has been determined using Sheninger method [5–6].

IR spectrums of polymer mixtures and compositions have been taken at HR-20 IR spectro-photometr in 400–4000 sm^{-1} area.

Determination of physico-mechanical properties of vulcanizates has been carried out according to the standarts. Preparation of samples has been carried out in the laboratory condition within 12 minutes at 90 °C temperature. The obtained compositions after heating at 153 °C within 30 minutes, under 6 Mpa pressure, have been extracted with dichlorethane within 72 hours to be purified from modificated composition chlorine compounds.

Extracted samples have been dried till the free weight under 50–60 °C vacuum. Thermal stability of initial polymers and polymer mixture, have been studied at 10 °C/min temperature change rate, at 400 °C heating regime, and atmosphere air in dynamic condition in Kurnaov pirometer and «Paulic-Paulic Erdey» derivatograh system by differencial thermal and thermogravimetric method.

Role of functional group polymers-PVC, CCPE, SREPT-40, in the mixtures saturated by synthetic isoprene rubber has been learned to analyse properties of rubbers based on saturated rubbers with functional group polymers.

Functional group polymers mixture substituting main polymer has been introduced in 2.5.–3.0. mass quantity. 100 mass SRI, 1.0-stearicacid, 5.0 zink oxide, 0.6. altax, 3.0. – diphenyldiguandin, 1.0 mass sulfur have been added into the mixture.

Homogenous composition mixture has been vulcanizated at 133 °C within 33 minutes at the laboratory condition. Physico-chemical properties of the obtained vulcanizate have been determined and the results have been given in table 1. As it is seen from the table functional group polymers improve thermal durability of vulcanizates and their relation with metal.

Dynamic properties of vulcanizate worsen when the quantity of PVC in the mixture increases from 2.5 to 20 mass.

That is why it is recommended to introduct only 2,5 ÷ 5,5 mass PVC into the mixture.

Introduction of CCPE into the mixture till 30 mass increases fatigue resistance of vulcanizates in repeated formation.

Table 1.

Names	Content of mixtures,						
	1	2	3	4	5	6	7
SRI-3	9	97.5	95	99	95	99	95
CAPP	1.0	2.5	5	–	–	–	–
CCAPP	–	–	–	1.0	5.0	–	–
SCAPP	–	–	–	–	–	1.0	5.0
Properties of vulcanizate							
Indices	Properties of vulcanizate						
	1	2	3	4	5	6	7
Strength level in violation, MPa	24.4	19.7	15.3	22.1	15.8	21.7	15.0
Conditional tension in 300% elongation, MPa	0.96	0.92	0.63	0.90	0.65	0.87	0.67
Conditional tension in 500% elongation, MPa	1.81	1.70	1.31	1.79	1.25	1.81	1.27
Relative elongation,%	900	870	840	880	900	870	890
Relative residue deformation,%	9.1	9.0	10.2	8.5	8.0	9.0	8.5
Violation resistance,	38.0	35.1	27.0	40.0	28.0	38.5	31.5
Elasticity,%	70.0	68.0	61.5	68.0	62.0	69.0	63.0
Conditional solidity unit on TM-2	35.0	32.0	27.6	35.0	31.0	35.0	30.0
Heat aging coefficient at 100 °C within 72 hours	0.93	0.91	0.87	0.94	0.91	0.92	0.90
Relation stability of rubber with metal, MPa	1.13	1.19	1.21	1.09	1.45	1.02	1.35

Mixture content- mass stearic acid-1.0; neozon D-1.0; santolex Up-0.5; N-nitrozodifenylamine-0.7; rubrax-5.0; modificator-Pv-1–1.5; captax-2.0; sulfenamid. TC-1,2; microfoste-2.0; technical carbon-P-514–45.

Mixture plasticity changes at 0.59–0.64 interval.

Adding SREPT-40 and SREPT-60 into the mixtures based on SRI-3 rubber and functional group polymers increases cohesion ability of these mixtures. Analysis has been shown that SREPT quantity in this mixture must be 5÷ mass.

Table 2. – Physico-mechanical properties of vulcanizates of SPI based rubber mixtures

Names	Mixture content *				
	1	2	3	4	5
SRI-3	85	85	85	85	85
SREPT	10	10	10	10	10
CCPE	5	5	–	–	–
PVC	–	–	2.5	5	5
PH-6 Ş oil	0.45	0.45	0.45	0.45	0.45
thiuran	2.0	2.0	2.0	2.0	2.0
sulfur	2.0	2.0	2.0	2.0	2.0

With this purpose rubber based on SRI-3 and SREPT has been prepared and physico-mechanical properties of the mixture vulcanizate have been learned.

SRI-3 rubber is added beforehand prepared SREPT mixture. The quantity of sulfur and thiuran in the mixture has been adjusted and as a result of carried out studies introduction of SREPT into the mixture in 2.0 and 0.45 mass was more efficient.

Prepared mixture has been vulcanized at $155\,^{\circ}C$ temperature within 15 minutes. Obtained results have been given in tables 2,3 and 4.

Table 3. – Physico-mechanical properties of vulcanizate

Indices	Properties of vulcanizates				
Violation strength level, MPa	19.3	18.1	19.7	20.3	18.0
Conditional tension in 100% elongation, MPa	3.4	3.1	3.2	3.4	3.2
Conditional tension in 300% elongation, MPa	10.5	10.0	10.8	11.2	10.5
Relative elongation,%	470	500	540	520	480
Relative residue deformation, %	67.5	65.0	63.5	62.8	60.0
Elasticity, %	41	40	44	45	42
Conditional solidity unit on TM-2	62	60	61	62	61
Heat aging coefficient at 100 °C temperature, within 72 hours	0.60	0.61	0.62	0.61	0.58
Relation stability with cord. (H-method) $*10^{-2}$ Cord 17 B 23 °C 100 °C 120 °C Cord 22 B 23 °C 100 °C 120 °C	 6.7 6.1 5.2 4.4 3.5 2.8	 6.3 5.9 7.3 4.0 3.2 2.9	 8.6 8.0 7.3 6.4 5.9 5.2	 8.0 8.4 7.6 6.7 6.2 5.4	 7.9 6.4 5.1 5.9 5.7 4.8

Some properties of the vulcanizates obtained on the base of SRI-3, SREPT, PVC are superior than production rubbers-solidity in violation, heat aging, relation stability with 17 B and 22 B cords and elc.

Use of 2.5 ÷ 5.0 mass quantity PVC in testing rubbers showed that physico-chemical properties of these rubbers including relation stability are more superior in SRI-3, SRMS-3, BMSR-25 than in the main rubbers.

It has been shown that rubbers based on 85 ÷ 87.5 mass SRI-3; 10 SREPT and 2.5÷5.0 mass PVS can be offered for tyre production.

Generalization of the obtained results show that according to repeated deformation fatigue, tension fluence: CCPP; CCaPP, – CAPP, CCPE-PVC.

According to the relation slability with metal (C_t-3) functional polymers have the following sequence.

Table 4. – Recipe of test rubbers prepared on the basis of rubbers and properties of their vulcanizates

Name	Content of mixtures, mass					
SRI-3	70	85	85.5	87	85	85
SRI-3 APKM-15	30	–	–	–	–	–
SRERT-60	1.0	5	–	–	–	–
CCPE	–	10	10	10	10	10
PVC	–	–	–	2.5	5	5
ПН-6Ш oil	4.0	–	4.0	–	–	4.0
tiuran	–	0.45	0.45	85	0.45	0.45
sulfur	2.2	2.0	2.0	2.0	2.0	2.0
Main indices of vulcanizates						
Violation strength level, MPa	21.1	19.6	18.7	19.9	20.1	18.2
Conditional tension in 100% elongation, MPa	2.5	3.6	3.4	3.1	3.3	3.3
Conditional tension in 300% elongation, MPa	9.2	10.9	10.2	11.0	11.6	14.0
Relative elongation,%	550	430	460	520	520	460
Relative residue deformation,%	26	19.5	19.0	19.0	20.0	18.0
Elasticity,%	43	42	41.5	46	47	40
Conditional solidity unit on TM-2	60	63	61.5	61	60	62
Heat aging coefficient at 100 °C temperature, within 72 hours	0.46	0.60	0.60	0.61	0.59	0.59
Relation stability with cord. (H-method) $*10^{-2}$ Cord 17 B 23 °C 100 °C 120 °C Cord 22 B 23 °C 100 °C 120 °C	 4.1 3.6 3.5 3.5 2.9 2.5	 6.8 6.2 5.1 4.2 3.4 2.6	 8.8 5.7 4.6 4.0 3.2 8.4	 9.3 7.6 7.0 6.5 6.0 5.7	 9.3 8.8 8.0 6.9 6.4 5.3	 8.1 6.5 5.0 6.2 5.8 4.4

PVC-CCPE-CAPP-CCAPP, – CCPP

According to vulcanizate heat durability:

PVC-CCPE-CCPP-CSAPP

According to the violation resistance functional polymers have the following sequence:

The results of the carried out scientific researches show that it is necessary to have general interphase relation to obtain rubbers with high physico-mechanical properties but the structure of the hetogenous vulcanization net is not important.

To improve interphase relation various additives have been added into polymer mixtures.

When in SRI-3, CAPP, CCAPP and SCAPP mixtures, the quantity of CAPP, CCAPP and SCAPP is 1.0 mass then the physico-mechanical properties of vulcanizates are good. Increase of relation stability of metal with the mixtures with 1÷5 mass CAPP, CCAPP and SCAPP is explained by the increase of mixture functionality.

It is recommended to add SREPT-40 and SREPT-60 elastomers to the mixtures based on CRI-3 rubber and functional group polymers to increase corrosion ability of these mixtures.

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Research of the influence of the modified carbon on the properties of rubber compounds

Abstract: The modified carbon is characterized by its difference of chemical compositions from known brands of low structural technical carbons, T 900, T 701, T 705, P 803, namely, with the increased maintenance of oxygen and hydrogen. Study of extraction products of modified carbon testifies to the presence of organic compounds, finish on a surface of carbon particles to 12 %. The element composition has been determined: carbon-92,11%, hydrogen-5,70% and oxygen-2,19 of %. Gross formula of extract is $C_{54}H_{40}O$. Average number molecular weight according to the gel-chromatography makes ≈ 700. Introduction of the modified carbon in composition of rubber compounds reinforces interphase interacting on boundary line «rubber-fillers» and formations of additional bonds between macromolecules of rubber and functional groups of oligomer, as a result, complex enhancement of properties of compositions is observed.

Keywords: carbon, properties, compositions, rubber compounds, elastomeric, plastic, elastic, structure.

Introduction. One of effective ways of improvement of properties of rubber compounds is application of new fillers different from structure and properties to which number refer to the modified carbon. Earlier [1] it has been shown that the modified carbon can be used in the capacity of filler by the manufacture of elastomeric compositions. Physical and chemical properties of modified carbon: specific conditional surface-19–24 m^2/g, specific adsorption surface on nitrogen (method BET) – 85–90m^2/g, Iodic number – 100–110 of mg/f, Absorption of dibutylphthalate – 170–180 ml/100 g, pH water suspension-6–8. Element composition: carbon-88–90%, hydrogen-3–4%, oxygen-6–7. Ash content – 0.8%. Apparent density-156 g/1000 sm^3. Average diameter of particles – 45–70 of nm.

Research objects and methods. The influence of the modified carbon, which is a secondary material of the manufacture of acetylene, on technological properties of rubber compounds on the basis of caoutchoucs SRI-3 and nairite KP-50 has been investigated. Investigated rubber stocks was contained modified carbon from 10 to 60 mass f. on 100 mass f.of caoutchoucs. For comparison the mixes loaded with technical carbon P 803 were taken.

Mixes were made on laboratory rollers, and also in the plenum chamber Plasticord Brabender of type РIУ-151 in volume of 75 sm^3 at a rotational speed of rotors of 30 min.$^{-1}$ and chamber initial temperature 343 ± 3 K. The extent of volume filling of the chamber made 70%. Fillers were input into the chamber after preliminary mastication of rubber within 3 minutes. On the gained dependences of a torque moment *of* M_t on a time from plastogramms parametre of workability (λ) was counted [2]. The extent of mastication of mixes $M_{max.}/M_{min}$, relative increment of the maximum torque moment at introduction of filler *of* $M_{rel.}$, conditional speed of mastication $V_{mast.}$ and the maximum value of temperature in mixing chamber $T_{max.}$.

Extrudability of rubber stocks was studied by means of an attachment, using dies d = 3 mm and tip "Garvey". Samples were extrude at a rotational speed of the screw of 20–120 min.$^{-1}$ and temperature 293–363 K [3].

Plastic- elastic properties of rubber compounds were defined in accordance with SS 1020–95-rigidity and elastic recovery of elasticity on Defoe; in accordance with SS 10722–94-viscosity on Mooney (ML4–373).

Results and discussion. In the course of mixture of rubbers with modified carbon *of* M_{tr} considerably increas-

es in process of filling of the chamber with materials and attains the maximum magnitude upon termination of loading and depressing of the overhead gate, then the twisting moment starts to decrease as a result of a leakage of processes of a mechanodestruction of a rubber phase of a mix, and also an increase of temperature in the chamber. On the basis of gained plastogramm, showing changes of torque moment in a time (16 min.), characteristics of rubber stocks (fig. 1) was counted. It was determined that in process of increase in the mixture time it is observed gradual rubbing in and absorption of filler by rubber. Thus the best rubbing in and filler absorption are observed in case of mixture of rubber with the modified carbon, than with technical carbon P 803. It proves to be true rather smaller value *of* M_t that in turn leads to the best workability and $M_{max.}/M_{min}$. Mixture process influences not only on filler type, but also on the elastomer nature. So, at filling up of SRI-3 by the modified carbon (to 40 mass f. on 100 mass f. caoutchouc) values λ and $M_{max.}/M_{min.}$ sharply decrease, and at further ($\geq$ 40 mass f.) raise of the maintenance of the modified carbon these values do not change practically. While at filling up of nairite KP-50 the modified carbon (to 40 mass f.on 100 mass f. caoutchouc) increases λ and $M_{max.}/M_{min.}$ decreases.
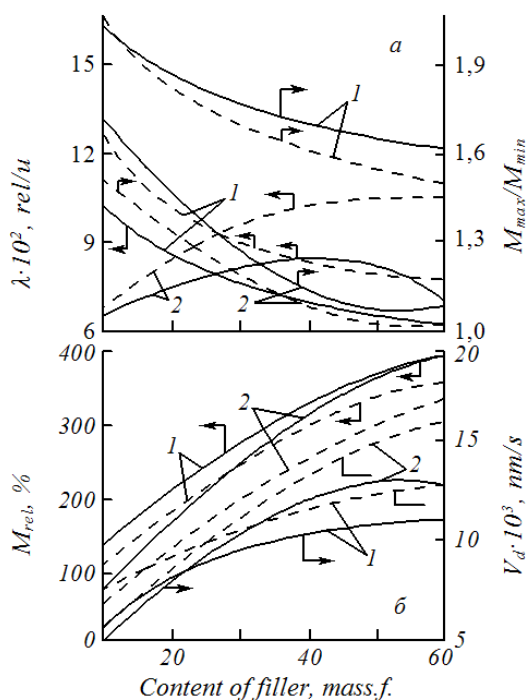

Figure 1. Workability change λ, plasticizing capacity $M_{max.}/M_{min.}$: (*a*), a relative torque moment of $M_{rel.}$ and masticating speed $V_{mast.}$ — (б) rubber stocks on the basis of rubbers SRI-3 (1), nairite KP-50 (2) depending on the maintenance of modified carbon (----) and technical carbon P. 803 (——)

At introduction of the modified carbon into the composition of elastomers it is also observed essential growth of $M_{rel.}$ and increase of V_{PA} (fig. 1,). Thus the character of change of $M_{rel.\ and}\ V_{mast.}$ depending on filling up extent is defined by a rubber phase of a mix and filler. For example,

$M_{rel.}$ and $V_{mast.}$ mixes on the basis of rubbers SRI – 3 and nairite KP-50 continuously increases with the growth of extent of filling up by the modified carbon and P 803 to 40 mass f. on 100 mass f. of cauchouc.

The mixes containing modified carbon, lead to rather smaller parametre of $M_{rel.}$ elastomer composition, especially in a case nairite KP-50. The conducted researches showed rather smaller rise of temperature of the chamber $(T_{max.})$ at raise of volume filling by a rubber stock with the modified carbon in comparison with P 803 (fig. 2).
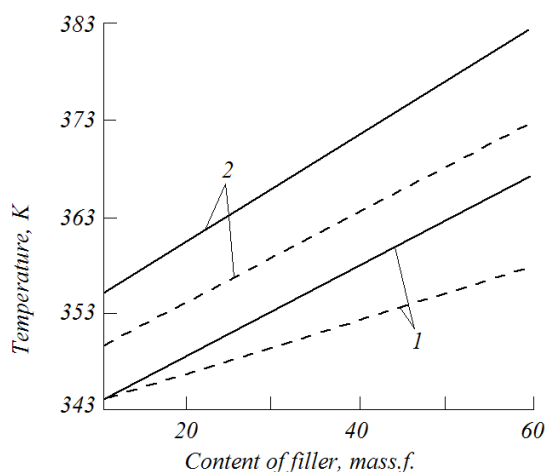

Figure 2.Changing of temperatures of the chamber in the course of mixture (for 15 min.) rubber stocks on the basis of SRI-3 (1) and nairite KP-50 (2) depending on the maintenance of the modified carbon (----) and technical carbon P 803 (——)

In the table the change of plastic-elastomeric characteristics of rubber stocks depending on the maintenance of the modified carbon is shown. From this table it is visible that with increase in the maintenance of the modified carbon in rubber stocks their rigidity, viscosity monotonously increases, plasticity and elastic recovery decreases. However on an absolute value of technological parametres the mixes containing modified carbon and technical carbon P 803 are discriminated among themselves slightly.

Table 1. – Plastic-elastic properties of rubber compounds on the basis of SRI-3 and nairite KP-50 filled by modified carbon and technical carbon P 803

Content of filler,	$ML_4 - 373$ K		P, rel. un.		RD, N		EL, mm	
mass. f.	SRI-3	KP-50	SRI-3	KP-50	SRI-3	KP-50	SRI-3	KP-50
МУ								
0	31	62	0,78	0,62	2,6	6,1	0,5	3,1
20	39	70	0.76	0,49	3	6,5	0,4	2,5
40	44	80	0,7	0,4	3,5	9	0.4	2,2
60	51	98	0,64	0,31	6	13	0,3	1,8
P 803								
20	39	69	0,7	0,55	3,1	7	0,3	2,1
40	42	78	0,64	0,42	4,5	10	0,3	1,8
60	49	90	0,62	0,38	5	17	0,2	1,6

Research of the extrudability of rubber stocks filled with modified carbon, showed that with increase in its maintenance pressure of a material of P_m in the extrusion head (essentially raises at P = const) (fig. 3). Quantitatively this effect is much less in comparison with P 803. For example, at 40 mass f. modified carbon and technical carbon P 803 on 100 mas. n. rubber SRI-3 and nairite KP-50 value of P_m makes 17,1 and 17,7 MPa, 18,2 and 18,8 MPa accordingly. Introduction of the modified carbon into the composition of elastomeric compositions also essentially changes the character of dependences of the volume charge of mixes at extrusion from pressure in head (fig. 4). Besides decrease in P_m in the presence of the modified carbon the slope angle, a straight considerably decreases and, hence, a heat release at extrusion in comparison with P 803. So, the maximum difference of temperature ΔT at processing of the rubber stocks containing 40 mas. n. The modified carbon and technical carbon P803 on the basis of SRI-3 and nairite KP-50, makes 16 and 21 °C, 18 and 24 °C accordingly. Consequently in the presence of modified carbon the probability of premature vulcanization of rubber stocks decreases and the possibility of an intensification of process of extrusion by increase in a rotational speed of the auger is provided.
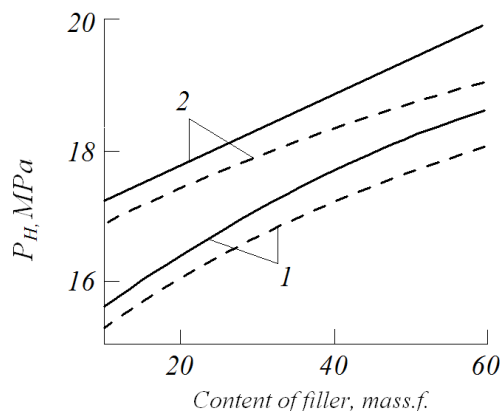
Figure 3. Changes of pressure in a head *(P_M)* at extrusion of rubber stocks on the basis of SRI-3 (1) and nairite KP-50 (2) depending on the maintenance of the modified carbon (----) and technical carbon P 803 (——) (T = 363 K, n = 120 min.⁻¹)

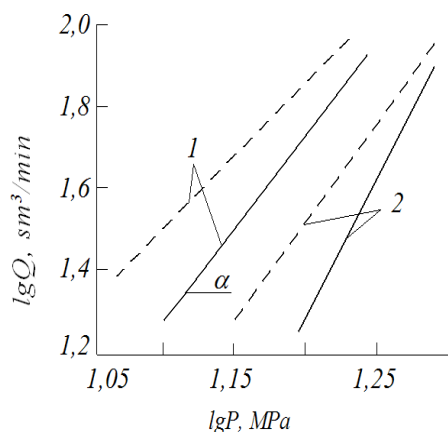Figure 4. The characteristics (dependence lg*Q*-lg*P)* process of extrusion of rubber mixes on the basis of SRI-3 (1), nairite KP-50 (2), containing 40 mass f. modified carbon (----) and technical carbon P 803 (——), (T = 363 To, *n* = 120 min.⁻¹)

The influence of the modified carbon on the capacity of rubber stocks to energy storage of elastic deformation at conversion was valued by measuring of an extent of extrudates swelling (ES). In fig. 5 it is shown the variation of ES of rubber compounds with the various maintenance of the modified carbon and technical carbon P803. It is visible that dependences have extreme nature. An optimum dosage of the modified carbon and technical carbon P803 in this case makes 40–50 mass f. on 100 mass f. of caoutchouc. Significant reduction of ES is observed in the mixtures containing modified carbon
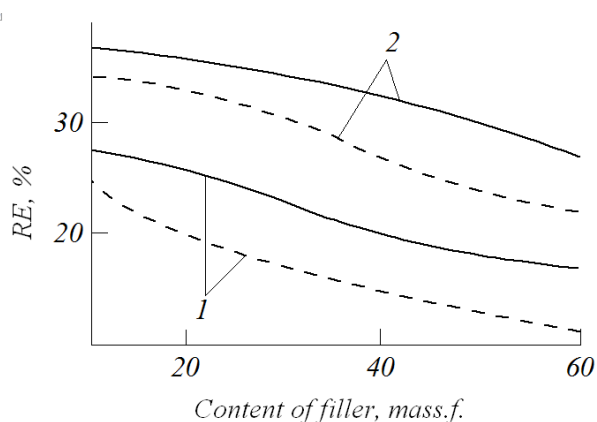

Figure 5. Change of extent of extrude swelling of rubber stocks on the basis of caoutchoucs SRI-3 (1), nairite KP-50 (2) from the maintenance of modified carbon (----) and technical carbon P 803 (——) *(T = 363 K, n = 120 min.⁻¹)*

Conclusion. Thus, the gained results show enhancement of technological properties of the rubber stocks filled with modified carbon in comparison with technical carbon P 803.

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Surfactants from the secondary intermediates used in oil and gas industry
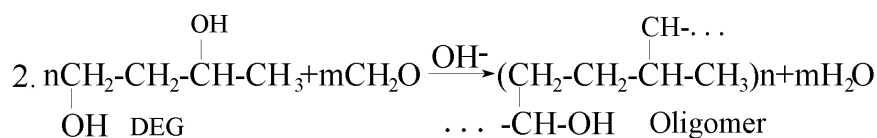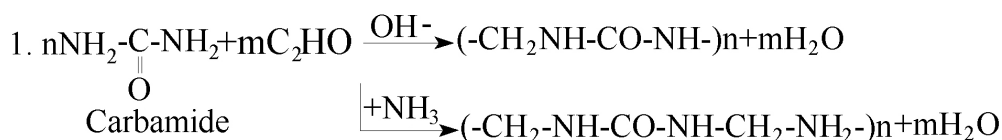
Abstract: In this article the scientific and practical experience and developed oligomers of polyols are readily soluble in water and exhibit surface-active properties of dispersed systems. Given surfactant successfully employed in oil and gas obtained from secondary intermediates chemical companies

Keywords: SAS, olygomers, GMTA, synthesis, demulsifiers, glycerin, oligomerization.

Amphiphilic surface-active agents (surfactants) are widely used in oil and gas production as emulsifiers, stabilizers, nucleators, demulsifiers and various disperse systems for effective management of their properties. The most selective nonionic surfactants are of species that differ in their colloid-chemical and other performance indicators, especially with dehydration and desalting of crude oils with commercial preparations to transport them for processing.

Technology for producing non-ionic surfactants are based on the esterification reaction of carboxylic acids with polyhydric alcohols oligomers. Oligomers polyhydric type "Laprol" alcohols were obtained by oligomerization of diethylene glycol (DEG) or diethanolamine butanediol with hexamethylenetetramine (GMTA) in alkaline medium.

Optimization of conditions for the above processes oligomerization polyols employing a laboratory setup with a change in temperature, time and ratio control, reacting the reaction components.
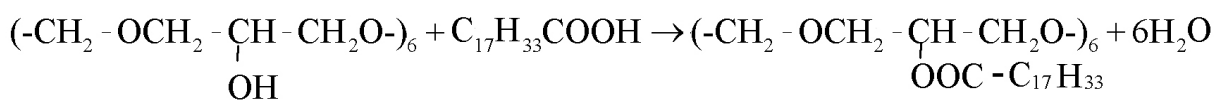
$$1.\ nNH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH_2+mC_2HO \xrightarrow{OH^-} (\text{-}CH_2NH\text{-}CO\text{-}NH\text{-})n+mH_2O$$

Carbamide

$$\xrightarrow{+NH_3} (\text{-}CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH_2\text{-})n+mH_2O$$

$$2.\ n\underset{OH}{CH_2}\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}CH_3+mCH_2O \xrightarrow{OH^-} (CH_2\text{-}CH_2\text{-}\overset{CH\text{-}\ldots}{CH}\text{-}CH_3)n+mH_2O$$

DEG   . . . -CH-OH   Oligomer

Yield glycerol oligomers, diethanolamine DEG with decomposition at GMTA $6CN_2O\ 4NH_3$ and at the given

conditions above are functional and adequate reactions are not due to differences in their reactivity. Moderate

alkaline reaction of oligomerization produces ammonia resulting from the decomposition of GMTA. Oligomerization reaction parameters and indicators of the reduced intermediates derived surfactants are comparable with the properties of their non-ionic species.

According to the results of the process of condensation of alcohols and dissimilar in the decomposition of urea GMTA formaldehyde and ammonia it is seen that the obtained water soluble oligomers with different values of the conversion obtained surfactants with different average molecular weights and functionalities. A characteristic feature of this reaction that proceeds with condensation reaction of the urea formaldehyde at 28% conversion calculation to take their number.

The synthesis of such nonionic surfactants with demulsifying properties of crude oils produced, as by oligomerisation followed by esterification with glycerol oligomer thereof with oleic acid.

In general, the oligomers obtained polyols are readily soluble in water and exhibit surface-active properties of dispersed systems.

Oligomerization trioksimetilenom glycerol (paraformaldehyde) is a polycondensation reaction under acidic conditions. Education hexamer of glycerine to the slow decomposition of the trimer trioxymethylene regulated catalytic effect of acid concentration and the ratio of reactants. When you set the optimal reaction conditions was obtained hexamer of glycerine:

Hexamers glycerin transparent, readily soluble in water, viscous liquid.

Nonionic demulsifier obtained hexamer ratio glycerol: oleic acid = 3: 1. Hexamer glycerol esterified oleic acid with vigorous stirring and heating at 240 °C for 5 hours.

$$(\text{-CH}_2 - \text{OCH}_2 - \underset{\overset{|}{\text{OH}}}{\text{CH}} - \text{CH}_2\text{O-})_6 + C_{17}H_{33}\text{COOH} \rightarrow (\text{-CH}_2 - \text{OCH}_2 - \underset{\overset{|}{\text{OOC} - C_{17}H_{33}}}{\text{CH}} - \text{CH}_2\text{O-})_6 + 6H_2O$$

Said glycerol ester (hexamer) with oleic acid exhibits surface active properties: 0.5% aqueous solution reduces its top-surface-tension at s = 43din/cm and forms a stable foam (4 cm3) Techa-nii 10 minutes. The resulting pale red paste highly soluble in water and oils, with 0.5% oil emulsion with a nonionic emulsifier is destroyed by 92% and effectively exfoliates.

Table 1. – Chemicals used in «Mubarekneftegaz» oil-gas refinery

№	Chemical name and their labeling	Where and in what cases used these chemicals	Where produced (country)	Annual consumption of chemical reagents, ton/year	Reagent costs in US Dollar
1	Dodikor-4345	Corrosion inhibitor	Germany	206,9	3180,6
2	Dodikor-4713	To keep the low pressure in the system	Germany	550,0	2090,0
3	Clariant	For the production and storage of oil	Germany	467,0	3100,0
4	Diethilenglycole (DEG)	For the dehydration of natural gas	UK	1625,9	1354,9
5	K-1 (nonionic SAS)	Demulsifier for gas condensate preparation	China	40,1	2200,0
6	V-2879 K (catyionic SAS)	An inhibitor against salt formation	Germany	340,3	2080,0
7	K-1 and Dissolvan 4411	Water oil-soluble demulsifier of oil	China, Germany	203,5	1770,0 (EUR)

In preparing the emulsified oil with the water in the tanks of their pretreatment for UDP fields «Mubarekneftegaz» foreign chemicals, various production including demulsifiers (Table 1).

Preparation of gas condensate and oil in the fishery is carried Kokdumalak import deemulgatorom – «K-1» Chinese production.

Table 2. – SAS technology is used preparation of oil and gas condensate fields in the «Mubarekneftegaz» oil-gas fields

№	Description of SAS	Type	Annual consumption, ton/year	Price, sums/ton	Amountmln SUM	Where used
1	Imported dumilsifier (China)	«K-1»	232,0	3951239	916,68	At the preparation of oil and gas condensates stations,.
2	Scale inhibitor (Germany)	«VI-2870 K»	140,0	2447049	342,580	At the stations of oil dehydration.
3	Dehydrating agent (Russia)	DEG	1600,0	1363265	2181,28	With preliminary gas preparation.

* – consumption of 2005, now increased for 1,5 times

In such cases, a dehydration dispersing brine water from oil and gas mixture in the pre-separator (SP-1), where its contents are reduced to 3.5–5.5%, with the presence of well-tional crystallization of water. This dispersion of the water-oil-gas emulsion is destroyed, stratified and can be interlocked with a solution of an effective emulsion breaker. Thus its concentration in the oil should not exceed 100 g/m and does not affect the quality of the oil obtained from them. Also reagents demulsifiers and desalting of crude oils used in oil and gas production series surfactants and water-soluble polyelectrolytes having cobuilder properties and dispersion properties of clay stabilizer solutions.

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Pharmacological activity and studying of the chemical compound of Hypoglycemic Gathering

Abstract: Researches are carried out on studying of a chemical composition of new hypoglycemic gathering including leaves of a big plantain and the white mulberry, in which result the complex of dietary supplement causing its specific activity has been established. The obtained data are used for a substantiation of system of standardization of gathering.

Keywords: gathering, hypoglycemic, a mulberry, a plantain, qualitative reactions, chromatographic analysis, quantitative definition, standardization, authenticity, polyose.

Public health care, improvement of medicinal supply is one of the main tasks of our state in the field of social policy. The decision of this problem in in a greater or lesser degree depends on working out and practical application of public health services of new effective medical products, including a phytogenesis. Thereupon revealing, studying and application of new perspective plants of domestic flora is represented as an topical issues of a pharmaceutical science.

Despite of application of new effective medical products with hypoglycemic effect, diabetes treatment remains an topical issue for applied medicine. It is connected with presence of some by-effects, contra-indications for use of synthetic preparations of various chemical groups. Thereupon it is expedient to use herbs in complex treatment of a diabetes along with the basic medicamentous therapy [1].

As we know, hypoglycemic effect of herbs is caused by presence of glycocinanes which are easily digested by organism and activate regenerative processes, reducing sugar level in blood [2–4].

Considering these circumstances, structure of hypoglycemic gathering including leaves of big plantain (PlantagomajorL.) and white mulberries MorusalbaL.) have been developed.

The purpose of the present research is studying of pharmacological effect and a chemical compound of new hypoglycemic gathering for the purpose of definition of basic biologically active substances.

Experimental part

For introduction of a new preparation of hypoglycemic effect in medicine practice, influence of it to physiological level of blood, and to the sugar content in blood at hyperglycemia caused by the glucose has been studied. The serial samples of gathering were used for analysis which prepared according to instructions of article "Gathering" GF of XI edition [5] is used. Medicinal vegetative raw materials were crushed separately till the size of the particles which are passing through a sieve with apertures in diameter of 2 mm. Then the dust was eliminated through a sieve with apertures in the size by of 0,25 mm. Further components were weighed and mixed up to getting uniform mass.

Infusions from gathering (1:10) were prepared according to the requirements of article GF XI "Infusions and broths" and used fresh prepared. Studying of influence of hypoglycemic effect to physiological level of blood was defined by a technique [27, 29] on 12 rats by mass of 140–160 gram.

Rats within 7 days contained in conditions of vivarium. Before experience rats were weighed and initial concentration of sugar in blood was defined. Blood was taken after a placing of animals into the special chamber — "small house" for an exception of excessive excitement. After establishment of initial concentration of glucose in blood rats were divided to two groups on 6 pieces in each one. 1st group was control and received water in volume of 1,5–1,7 ml per os, to second experimental group water infusion of hypoglycemic gathering was entered inside by automatic probe in a dose of 10 ml/kg unitary. Through 60 and 120 minutes after oral injection of the examined solution they defined sugar level in blood of rats. They made sugar definition in blood with application of a standard set of firm «ECO — lab» of Russia by glucose oxidase method. Measurement of optical density of probes made at KFK device. The received results are processed statistically. Sacchar decreasing effect of hypoglycemic gathering (HG) also is studied on model of hyperglycemia caused by loading of high doses of glucose on the technique on 12 rats of mass of 150–170 g.

Results of studying of effect of gathering to physiological level of glucose in blood at rats are presented in table 1.

Table 1. – Effect of hypoglycemic gathering to physiological level of glucose in blood of rats (M±m, n=6)

Experiment condition	Initial n=6	HG 1st hour	HG 2nd hour	
Content of glucose in blood, mmol/l	6,00 ± 0,38	6,65 ± 1,14	4,65 ± 0,43	P < 0,01

Apparently from the table, initial concentration of sugar in blood of rats is equal to 6,00 ± 0,38 mmol/l., unitary insertion of hypoglycemic gathering caused doubtful increase of level of sugar of blood at the first hour after resorption. At 2nd hour decrease in level of sugar in blood of experiment rats to 22,5% is revealed in comparison with initial concentration of glycaemia at rats.

Results on studying of effect of hypoglycemic gathering to glucose level in blood at hyperglycemia are presented in table 2.

Table 2. – Effect of hypoglycemic gathering to glucose level in blood ofrats at hyperglycemia (M±m, n=6)

Experiment conditions	Initial n=12	Control (glucose)	HG + glucose	
Content of glucose in blood, mmol/l	4,56 ± 0,38	10,43 ± 1,14	7,21 ± 0,43	P < 0,01

Apparently from table 2, initial concentration of sugar in blood of rats is equal to 4,56 ± 0,38 mmol/l; the glucose injection has led to increase of level of sugar in blood of control rats more than to 2,2 times. In similar conditions in 2nd hour after reception of infusion of gathering in blood of experimented rats decrease in sugar of blood to 7,21 ± 0,43 mmol/l is noticed, that more low than control level to 30,8%. The obtained data testify

to inhibition of hyperglycemic reactions of an organism to insertion of exanthropic glucose.

For definition of a chemical structure of gathering its preliminary research on the content of the basic groups of biologically active substances is carried out with use of well-known qualitative reactions and chromatographic methods of the analysis [6–10].

For acknowledgement of the received results and identification of the found out substances comparative chromatographic studying of extraction was held where these substances have been revealed, with corresponding extraction of initial components of gathering in the presence of authentic samples – "witnesses". At visual comparison of chromatograms before and after processing with chromogenic reactants the big similarity on a set of biologically active composites in extraction of gathering and its components differing only in a size and with intensity of spots in ultraviolet – light is revealed.

At chromatograph of water extraction on a paper (German, of FN-3 Mittelschnelllaufend brand) in system of solvents butanol-acetic acid – water (4:1:5) presence of the following substances has been confirmed:

– ascorbic acid (Rf 0,42, developer – Tilmans reactant);

– organic acids: lemon (Rf 0,48), apple (Rf 0,57), oxalic (Rf 0,62), succinic (Rf 0,6) (developer – 0,04% a solution bromo-phenol blow);

– the free sugars presented by glucose (Rf 0,49), maltose (Rf 0,30), fructose (Rf 0,63), sucrose (Rf 0,38) (developer – Folling reactant).

Polyoses from water extraction are allocated with sedimentation by ethanol. Monosaccharide structure of polyoses were defined after hydrolysis [11]. Hydrolysis of 0,05 g of absolutely dry polyoses were held with 2,5 ml of 2 mol/l of a solution of sulfuric acid on a boiling water bath during 8 hours. After neutralization of barium by a carbonate hydrolyzate was processed with cation exchange resin KУ-2 (H+-form), concentrated and was chromatograph simultaneously with authentic samples on a paper in systems of butanol-piridin-water (6:4:3) for neutral sugars and etilatsetat-acetic acid- ant acid-water (18:3:1:4) for sour sugars. For detection of sugars they used a sour solution of aniline phthalate and thermal processing. As a result of chromatographic analysis it is established, that polysaccharide gathering complex includes neutral monosaccharides: D-glucose, L-fructose.

In hexane extraction by a method of narrow-ringed chromatography on plates of «Silufol UV-254» in a system hexan-diethyl aether (17:3) 3 substances of lu-

tein nature, shown in the form of stains of dark blue color on a flavovirent background after processing with 10% spirit a of phosphatomolybdic acid solution and warming up at temperature 60–80⁰ C also has been found out. At comparison to the authentic sample one of the found out substances (Rf 0,48) were identified with β-carotin.

For definition of coumarins samples of gathering were extracted with 95% of ethanol on a cold during 24 hours. Then extraction was centrifugated with speed of 4,5 thousand rpm during 7 minutes, decant and chromatographed on plates of «Silufol UV-254» in system of geksan-etilatsetat solvents (3:1). At survey of dried chromatogram in Uf-light 2 spots with Rf 0,14 and 0,46, having bright-blue fluorescence and giving positive reaction with Pauli's reactant are revealed. It has allowed to carry the found out substances to coumarins.

For allocation phenol carboniferous acids, spirit extract of vegetative gathering were chromatographed on a column with polyamide sorbite. Elution was made by water; the received fractions investigated by means of a chromatography on a paper. The fractions containing phenol carboniferous acids were united. From acidified up to pH 3 of water eluate phenol carboniferous acids took with acetic ether. Then acetic ether extraction were boiled off and the rest were chromatograph in system of solvents of benzene- ethyl-carbonic acid- water (2:2:1). At display of chromatogram diazotize sulfanilic acid it is defines presence not less than 4 phenol carboniferous acids from which 3 are identified by comparison to authentic samples of substances (benzole Rf 0,25, gallic Rf 0,28, salicylic Rf 0,30).

For definition of flavonoids, spirit extraction of the gathering received in the way described above, were subjected to chromatographic research on a paper (German, of FN-3 Mittelschnelllaufend brand) in system of solvents of 15% acetic acid and butanol- acetic acid-water (4:1:5). In similar conditions division of authentic samples ("witnesses") was made. Flavonoids were defined on character of fluorescence in Ultraviolent -light before processing by chromogenic reactants (ammonia steams, spirit solution of hydrated oxidea sodium, 1% of spirit solution of chloride aluminum) and comparison of values of Rf found substances and authentic samples. Identification of flavonoids on chromatograms were held also by entering of obviously known composite into an initial extract. Thus they observed strengthening of a corresponding spot.

Results of the analysis are given in table 3.

Table 3. – Color reactions and data of chromatographic analysis with
flavonoids composites of hypoglycemic gathering

№	Value of Rf in systems		1% solution of AlCl₃ in fermentation alcohol	5% aqueous solution of sodium hydroxide	The nature of fluorescence In Ultraviolet-light		identified flavonoids
	БУВ (4:1:5)	15% CH₃COOH			Before processing by ammonia vapor	After processing by ammonia vapor	
1.	0,45	0,14	pale-yellow	yellow	yellow	yellow	rutin
2.	0,55	0,35	pale-yellow	canary	brilliant green-yellow	canary	hyperoside
3.	0,78	0,02	pale-yellow	yellow	canary	canary	meletin

Results of detection and identification of biologically active substances of hypoglycemic gathering are given in table 4.

Table 4. – Chemical components of hypoglycemic gathering

Analyzed groups	analysis result
Carbohydrates:	
Sugar (glucose, maltose, fructose, sucrose)	+
Water-soluble polyose	+
Vitamins (ascorbic acid, carotenoids)	+
Organic acids (lemon, apple, oxalic, amber)	+
flavonoids (routines, meletin, hyperoside)	+
phenol- carboxylic acids	+
(benzole, gallic, salicylic)	+
Coumarins	+
Tannins	+
Essence	+
Alkaloids	–
saponins	–

From data given in the table it is followed that hypoglycemic gathering contains the basic groups of biologically active substances, characteristic for its initial components — leaves of a big plantain and white mulberries.

Further researches under the quantitative content of biologically active substances are carried out.

The quantitative content of essence, tannins, ascorbic acid and free organic acids defined by the technique stated in HG XI [5]. The content of flavonoids of gathering was defined spectrophotometric, saponins — on indicator of foam number, phenol- carboxylic acids by gravimetric method. The content of other biologically active substances was defined by well-known technique [11–14], in particular, sugars — on method of Frsenius [15], coumarins on method of Nikonov G. K and coauthors [16].

Results of quantitative definition of the basic groups of biologically active substances of hypoglycemic gathering are generalized in table 5.

Table 5. – The quantitative content of biologically active substances in hypoglycemic gathering

Biologically active substance	Content,% to absolute dry weight
1	2
Carbohydrates:	
– monosaccharide	5,35 ± 0,12
– water-soluble polyose	9,3 ± 0,3
Vitamines:	
– ascorbic acid, mg%	110 ± 2,06
– carotenoid, mg%	3,3 ± 0,50
organic acids	1,68 ± 0,22

1	2
aspic oil	mark
flavonoids	0,4 ± 0,10
coumarins	0,05 ± 0,10
phenol-carboxylic acids	0,25 ± 0,09
tanning agents	4,50 ± 0,40

Conclusions: results of the conducted researches have shown, that hypoglycemic gathering causes decrease in level of sugar in healthy rats, and also at hyperglycemia caused by loading of high doses of glucose. Also at studying of a chemical compound of new vegetative gathering the complex of biologically active substances causing its specific activity is established. The obtained data have been used for a substantiation of system of standardization of gathering.

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Synthesis of 2,5-dihydroxy-ω-chloroacetophenones

Abstract: This paper reports a synthesis of 2,5-dihydroxy-ω-chloroacetophenone as a catalyst using $MoCI_5$, WCI_6, $SnCI_4$, VCI_3. The mechanism has not been studied. It was studied the influence of the ratio of reactants, catalysts' concentration and the time of synthesis in the reaction of obtaining 2,5-dihydroxy-ω-chloroacetophenone from hydroquinone and chloracetyl chloride. The purified 2,5-dihydroxy-ω-chloroacetophenone is characterized in terms of physical-chemical properties.

Keywords: 2,5-dihydroxy-ω-chloroacetophenone, chloracetyl chloride, small quantities Lewis acids, IR spectrum.

2,5-Dihydroxy-ω-chloroacetophenone is an aromatic ketone formula $C_8H_7O_3CI$ and an important photochemical reaction used in perfumery and as a reagent in organic chemistry. 2,5-Dihydroxy-ω-chloroacetophenone acts as an optical filter being able to use the energy of UV radiation (promoting electrons into an excited state) and release this energy as heat to the environment (electrons returning to the initial state). This is possible because 2,5-dihydroxy-ω-chloroacetophenone singlet and triplet have close states in terms of energy. 2,5-Dihydroxy-ω-chloroacetophenone is used as a flavor ingredient, a flavor enhancer, perfume fixative in perfumery industry. In the composition of perfumes, cologne and scented soaps and UV light does not degrade the smell and color of these products. It is used as an additive for plastics, coatings and adhesive formulations [1, 168–179]. It is a component of sunscreen products and a plastic packaging can be added to block UV rays, protecting products within them. It is used in textile to protect them against degradation under the action of ultraviolete radiation [2, 1–7]. In preparations for solar protection, 2,5-dihydroxy-ω-chloroacetophenone is intended to absorb UV-A and UV-B, protecting the skin from the negative effects of tanning (sun). It is known that structure is unstable in terms of photochemical because under the influence of sunlight it forms reactive radicals, aggressive, in which scientists associates with oxidative stress in human cells, skin damage, etc. 2,5-Dihydroxy-ω-chloroacetophenone and its derivatives are used as intermediates for dyes, in the manufacture of insecticides and pharmaceuticals, etc. In the pharmaceutical industry are used for their anesthetic and anti-inflammatory properties etc. [3, 1075–1076]. It is a white solid with the smell of rose, insoluble in water but soluble in benzene, tetrahydrofuran, methanol, and propylene glycol. 2,5-Dihydroxy-ω-chloroacetophenone and its derivatives are synthesized by Friedel-Crafts reaction of aromatics. Acylation is done with acid chlorides or anhydrides. The reaction is catalyzed by Lewis acids, BF_3, $AlCl_3$, $FeCl_3$, $TiCl_4$ or $ZnCl_2$ [4, 689–701]. Nowadays, restrictions are imposed for waste minimization requiring the development of new catalytic technologies often based on solid catalysts. Various research groups have reported the use as a catalyst of the Friedel-Crafts acylation of hydroquinone derivatives of various different metal oxides, for example a mixture of thorium dioxide, magnesium oxide, ZnO, etc. Friedel-Crafts reaction of hydroquinone and chloracetyl chloride in the presence of Lewis acid type catalysts ($AlCl_3$) or $MoCI_5$, WCI_6, $SnCI_4$, VCI_3 is used for the preparation of 2,5-dihydroxy-ω-chloroacetophenone (Scheme 1).
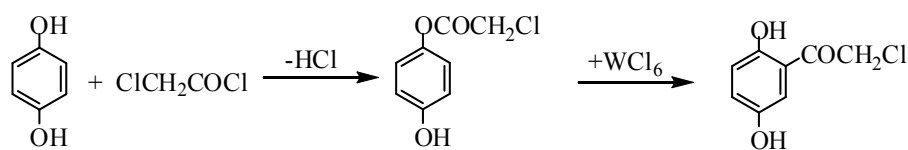
Reagents and materials

The reagents used were: hydroquinone (99%), chloracetyl chloride (98%), $MoCI_5$ (98.5%), WCI_6 (99%), $SnCI_4$ (99%), VCI_3 (99.5%). Merck, Sigma Aldrich. In this paper

reagents are used as such without further purification. Concentrated hydrochloric acid (37%) Sigma Aldrich, carbonyl sulphide and other materials are used without special treatment. Melting point determination is made using the device "Melting Point Meter" KRS-P1, the company Kruss Optronic GmbH. The IR spectrum was carried out using a Perkin Elmer FT-IR spectrophotometer – Spectrum 100.

Syntheses

In the syntheses with Lewis catalysts was used the classical method of synthesis. The work was done with hydroquinone, chloracetyl chloride, carbon disulfide, anhydrous aluminum chloride and the mixture was heated at 40–45 °C. In the syntheses where $MoCl_5$, WCl_6, $SnCl_4$, VCl_3 was used it was also used a catalyst system for stirring the reaction mixture in order to obtain the most intimate contact between the catalyst and the reactants. After completion of the synthesis the catalyst is removed by filtration ($MoCl_5$, WCl_6, $SnCl_4$, VCl_3). $MoCl_5$, WCl_6, $SnCl_4$, VCl_3 powder is reused after washing it with dichloromethane and dried. Crude 2,5-dihydroxy-ω-chloroacetophenone obtained after syntheses was purified by recrystallization from ethanol, filtered and dried under vacuum. Getting 2,5-dihydroxy-ω-chloroacetophenone is achieved by Friedel-Crafts reaction in the presence of $AlCl_3$ catalyst in good yields, and we tested the $MoCl_5$, WCl_6, $SnCl_4$, VCl_3 as catalyst. Laboratory syntheses were carried out in order to determine the influence of various parameters on the efficiency of the reaction of 2,5-dihydroxy-ω-chloroacetophenone: the variation ratio of the reactants, the variation in the catalyst concentration, reaction time, type of catalyst reaction.

The influence of the variation ratio of reactants

The syntheses were conducted with different molar ratios of the reactants chloracetyl chloride hydroquinone, ratios ranging from 1:1 to 1:2 and 1:3. The chloracylation is generally used, working at reflux. The reaction temperature is 136–138 °C. The concentration of $MoCl_5$, WCl_6, $SnCl_4$, VCl_3 catalyst was 0.2% compared with chloracetyl chloride. The reaction is given by the excess hydroquinone. The duration of the synthesis is 3 hours. In Table 1 is shown the variation of the yield depending on the ratio of reactants. As may be seen in Table 1 the yield increases with the increasing molar ratio of reactants. By working with a large excess of hydroquinone (molar ratio chloracetyl dechlorinated hydroquinone) of 1:3 is obtained a high yield of 91% of 2,5-dihydroxy-ω-chloroacetophenone. Using a large excess of one reactant leads to increased reaction yields, but increases are not very spectacular and taking into account the need for recovery of hydroquinone leading to increased costs it would be preferable to work with a ratio of chloracetyl chloride: hydroquinone 1:2.

Influence of changes in concentration of the catalyst

To track variation's influence the concentration of $MoCl_5$, WCl_6, $SnCl_4$, VCl_3 catalyst use the following values: 0.001%, 0.002%, 0.005%, 0.01% (percentage by mass) from chloracetyl chloride. Synthesis duration is two hours. Temperature is 136–138 °C. All syntheses were carried out with a molar ratio of chloracetyl chloride: hydroquinone 1:2. The results are shown in Table 1.

Table 1. – Chloracetylation of hydroquinone in the presence of small quantities of $MoCl_5$, WCl_6, $SnCl_4$, VCl_3

№	Molar ratio of hydroquinone: chloracetyl chloride: katalysator	Reaction time, hour	Temperature,° C	Yield,%	Reaction product by column chromatography,%	
					4-HPCA[*]	2,5-DHCA[**]
1	2	3	4	5	6	7
1	MoCl $1:1:2,5.10^{-3}$	3	136–137	82	9	91
2	$1:1:5.10^{-4}$	2	136–137	91	21	79
3	$3:1:1,2.10^{-2}$	2	137–138	76	26	74
4	WCl $1:1:5.10^{-3}$	3	136–137	80	28	72
5	$1:1:3.10^{-3}$	3	136–137	84	18	82
6	$3:1:7,4.10^{-3}$	2	137–138	75	30	70
7	SnCl $1:1:1,1.10^{-3}$	3	136–137	83	22	78
8	$1:1:2,2.10^{-3}$	3	136–137	85	33	67
9	$3:1:7,4.10^{-3}$	2	137–138	68	49	51

1	2	3	4	5	6	7
	VCI$_3$					
10	1:1:1,4.10^{-3}	3	136–137	62	29	71
11	1:1:2,8.10^{-3}	3	136–137	74	34	66
12	3:1:1,6.10^{-3}	2	137–138	57	36	64

* – 4-hydroxyphenylchloracetate

** – 2,5-dihydroxy-ω-chloracetophenone.

Watching the graph in Table 1 shows that with increasing concentration of catalyst (MoCI$_5$, WCI$_6$, SnCI$_4$, VCI$_3$) increases the reaction yield, but the yield is very small increased after increasing the concentration from 0.2 to 1% yield increase by only 9%. It is therefore preferred to work with a concentration of catalyst (MoCI$_5$, WCI$_6$, SnCI$_4$, VCI$_3$) of 0.002%.

The influence of reaction time

The observation of the influence of reaction time on the 2,5-dihydroxy-ω-chloroacetophenone synthesis by the Friedel-Crafts reaction in the presence of catalytic MoCI$_5$, WCI$_6$, SnCI$_4$, VCI$_3$ synthesis was accomplished by carrying out the reaction at different times. It increases the reaction time from 1, 2, 3 and 5 hours. The concentration of catalyst working with is 0.002% MoCI$_5$, WCI$_6$, SnCI$_4$, VCI$_3$ related to the amount of chloracetyl chloride. Synthesis temperature is the reflux (136–138 °C). The synthesis was carried out with a molar ratio of the reactants: Chloracetyl chloride: hydroquinone 1:2. Low yield of the reaction is observed after one hour of synthesis. With increasing reaction time and yields are higher, but the increase is not significant. After 5 hours of synthesis the yield of 2,5-dihydroxy-ω-chloroacetophenone obtained practically is 91%. The influence of the catalyst type on the yield of reaction The influence of catalyst type synthesis by the reaction of 2,5-dihydroxy-ω-chloroacetophenone Friedel-Crafts acylation has been found by working with the acylation catalysts AlCl$_3$ as compared to the catalytic action of MoCI$_5$, WCI$_6$, SnCI$_4$, VCI$_3$. The reaction time is 3 hours. The concentration of catalyst which is employed is 0.002% related to the amount of chloracetyl chloride. Synthesis temperature is the reflux. The MoCI$_5$, WCI$_6$, SnCI$_4$, VCI$_3$ synthesis with synthesis temperature is 136–138 °C. When working with AlCl$_3$ catalyst, the reaction temperature is 40–45 °C, because it is currently working in the reaction of solvent carbon disulfide. (40% by mass in relation to the reaction mixture). The syntheses were carried out with a molar ratio of the reactants: chloracetyl chloride: hydroquinone 1:2. Synthesized 2,5-dihydroxy-ω-chloroacetophenone was processed. In the first stage of the reaction mixture is filtered to remove the catalyst MoCI$_5$, WCI$_6$, SnCI$_4$, VCI$_3$. Then the clear solution is treated with water. Solution is treated with hydrogen chloride and passed into a separating funnel to separate the organic layer containing 2,5-hydroxy-ω-chloroacetophenone. The solution is heated to remove the excess hydroquinone. The resulting crude in the synthesis of 2,5-dihydroxy-ω-chloroacetophenone was made subject to a process of recrystallization for obtaining a pure compound. As the recrystallization solvent used is ethanol. 2,5-dihydroxy-ω-chloroacetophenone obtained and purified by recrystallization has been characterized from the physical-chemical point of view, the results are as follows: white crystals m. p. 63 °C, density 1.1 g/cm^3. 2,5-Dihydroxy-ω-chloroacetophenone is soluble in alcohol, chloroform, ether, and very slightly soluble in water. In the IR spectrum can be observed some characteristic absorption bands (Figure 1).

The FT-IR spectrum of crystal 2,5-dihydroxy-ω-chloroacetophenone shows bands characteristic to υC – H stretching vibration at 3072 cm^{-1} aromatic (m) and 3011 cm^{-1} (m) respectively the characteristic band of deformation at δC – H 1441 cm^{-1} (s). Bands characteristic to υC = C stretching vibrations assigned to aromatic ring at 1598 cm^{-1} were confirmed at 1598 cm^{-1} (i), and between 947–769 cm^{-1} appears characteristic bands to δC-H bending vibrations (characteristic to aromatic nucleus). At 1759 cm^{-1} band appears very intense band attributed to υC = O stretching vibration (for ketones). In the spectrum appear intense and very intense bands at 1298–1145 cm^{-1}range, assigned to the stretching vibrations υC – O.

Interesting results have been obtained in the synthesis of 2,5-dihydroxy-ω-chloroacetophenone as a catalyst using MoCI$_5$, WCI$_6$, SnCI$_4$, VCI$_3$. It is a heterogeneous catalyst which may be easily separated from the reaction mixture and reused. It is not corrosive and does not produce secondary products. The mechanism has not been studied. It was studied the influence of the ratio of reactants, catalysts' concentration and the time of synthesis in the reaction of obtaining 2,5-dihydroxy-ω-chloroacetophenone from hydroquinone and chloride chloracetyl. A comparison was made between the

catalyst and catalysts' Friedel-Crafts chloracetylation classics: aluminum chloride, respectively. Under the same reaction conditions as those used in the synthesis of $MoCI_5$, WCI_6, $SnCI_4$, VCI_3 the yield was smaller than classical catalysts, which can be explained by a too low concentration of catalyst. The purified 2,5-dihydroxy-ω-chloroacetophenone is characterized in terms of physical-chemical properties.
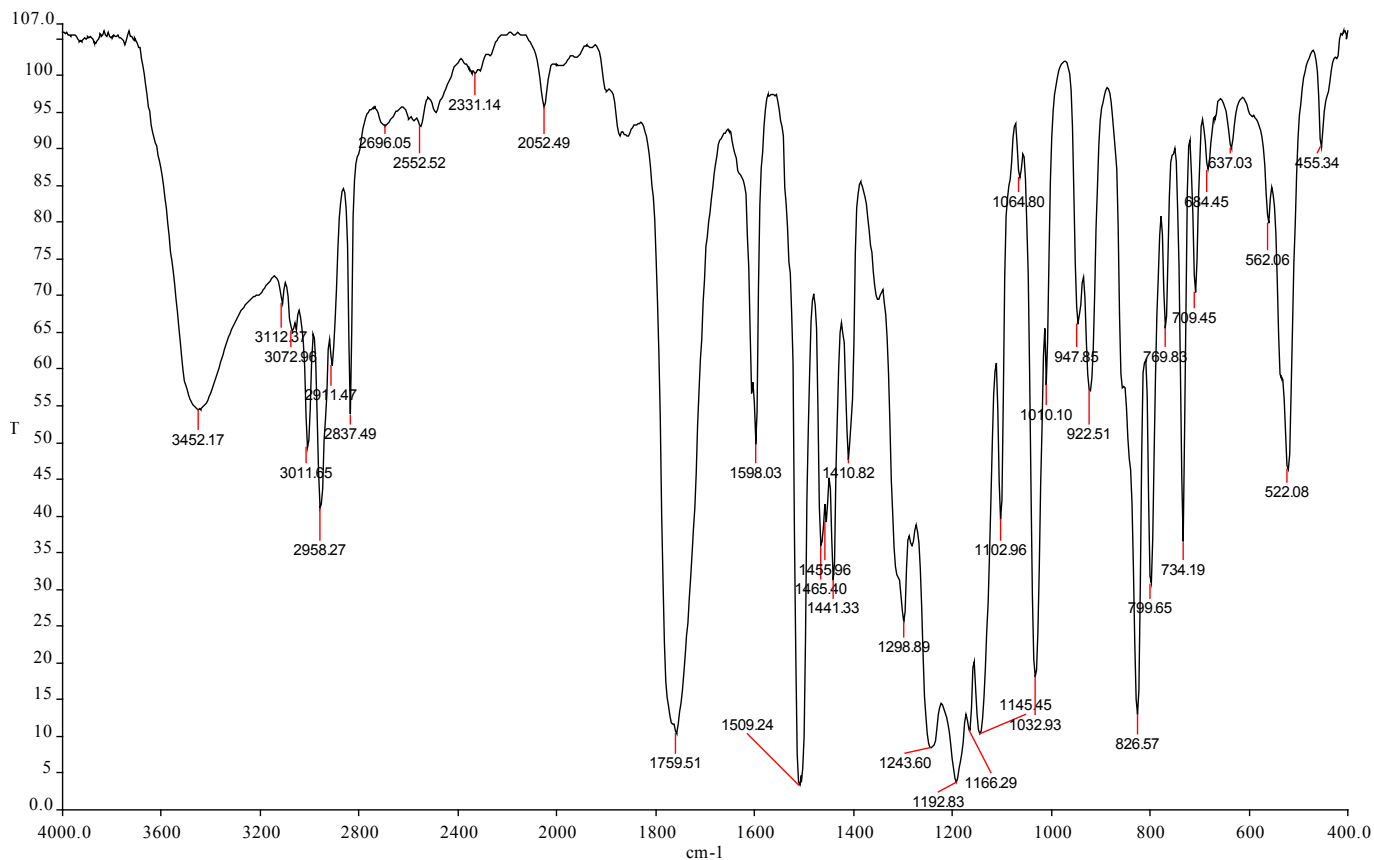

Figure 1. Is shown the IR spectra of 2,5-dihydroxy-ω-chloroacetophenone purified

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