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**PRODUCING OF LINOLEUM WITH IMPROVED PHYSICAL AND
MECHANICAL PROPERTIES**

**ПОЛУЧЕНИЕ ЛИНОЛЕУМА С УЛУЧШЕННЫМИ ФИЗИКО-
МЕХАНИЧЕСКИМИ ПОКАЗАТЕЛЯМИ**

G.F. Aminova, A.I. Gabitov, A.R. Maskova, B.R. Khusnutdinov,
L.K. Abdrakhmanova, R.F. Nafikova

FSBEI NPE “Ufa state petroleum technological university”,
Ufa, Russian Federation

FSBEI NPE “Ufa state petroleum technological university”,
branch, Sterlitamak, Russian Federation

АМИНОВА Г.Ф., ГАБИТОВ А.И., МАСКОВА А.Р., ХУСНУТДИНОВ Б.Р.,
АБДРАХМАНОВА Л.К., НАФИКОВА Р.Ф.

ФГБОУ ВПО «Уфимский государственный нефтяной технический
университет», Уфа, Российская Федерация

ФГБОУ ВПО “Уфимский государственный нефтяной технический
университет”, филиал, Стерлитамак, Российская Федерация

e-mail: asunasf@mail.ru

Abstract. A characteristic feature of the development of various areas of the industry is currently ongoing displacement of traditional metallic materials by plastics. Polyvinyl chloride (PVC) takes one of the leading positions. One of the reasons of extremely rapid growth of PVC production is the fact that there is not another polymer, which could be subjected to such modification varied as it is done with polyvinyl chloride.

It is caused by development of technological processes of production, increase of level of development of the equipment for polyvinyl chloride production, quality of raw materials and application of new compositions for achievement of necessary consumer properties of products. The uniqueness of PVC is that according on the production method, formulation and processing technology it provides a large range of polymer materials and products having different properties. For making articles elastic and for simplification of processing of polyvinyl chloride it usually plasticize, thus the content of softener reaches 40%. The most widespread of them are di (2-ethylhexyl) phthalate and dibutyl phthalate. Plasticizers diethylhexyl phthalate and dibutyl phthalate are used for plasticizing cable flexible PVC, linoleum, plastic construction profiles, decorative materials, artificial leather, technical films, products for food, medical and paint industries. However, the most widespread of all other industrial plasticizers dioctylphthalate relatively expensive and deficient. More affordable dibutyl phthalate has high volatility, which prevents its wide application. Therefore, despite the rather large range of plasticizers, their number is insufficient to meet the needs of modern industry. In this regard, the investigation of new plasticizers for PVC materials compositions is relevant and practically significant problem. This paper presents the research of preparation methods and physicochemical properties of oxyalkylated alcohols (butanol, 2-ethylhexanol and phenol) and phthalates on their basis, as well as test results alkoxyated alcohols phthalates as plasticisers in PVC compounding the top layer of linoleum. It is noted that the polymer compositions have a high melt flow values. As showed the conducted researches, PVC formulations of the upper layer of linoleum that we developed with the addition of plasticizers, meet the requirements of existing standards by all indicators, while using

butoxylalkylphenoxyalkylphthalate indicators such as petrol – resistance, % (1,25-1,53) and oil resistance, % (10,2-10,8), even superior to standard samples. Akoxylated alcohols based phthalates are potential PVC plasticizers.

Аннотация. Характерной особенностью развития различных областей промышленности в настоящее время является продолжающееся вытеснение традиционных металлических материалов пластмассами. Здесь поливинилхлорид (ПВХ) занимает одну из лидирующих позиций. Одной из причин чрезвычайно быстрого роста производства ПВХ является то обстоятельство, что пока нет другого полимера, который можно было бы подвергать такому разнообразному модифицированию, как это делают с ПВХ. Это обусловлено развитием технологических процессов производства, повышением уровня разработки оборудования для изготовления ПВХ продукции, качеством сырья и применением новых композиций для достижения необходимых потребительских свойств изделий. Уникальность ПВХ состоит в том, что в зависимости от способа получения, рецептуры и технологии переработки этот полимер дает большой ассортимент материалов и изделий, характеризующихся различными свойствами. Для придания изделиям эластичности и для облегчения переработки ПВХ его обычно пластифицируют, при этом содержание пластификатора достигает 40%. Наиболее широкомасштабными из них являются ди(2-этилгексил)фталат (ДОФ) и дибутилфталат (ДБФ). Пластификаторы ДОФ и ДБФ применяются для пластификации кабельного пластиката, линолеума, строительных полимерных профилей, отделочных материалов, искусственной кожи, технических пленок, изделий для пищевой, медицинской и

лакокрасочной промышленности. Однако, находящийся наибольшее распространение среди всех остальных промышленных пластификаторов диоктилфталат сравнительно дорог и дефицитен. Более доступный дибутилфталат имеет высокую летучесть, что препятствует его широкому применению. Поэтому, несмотря на достаточно большой ассортимент пластификаторов, их количество недостаточно для полного удовлетворения потребностей современной промышленности. В этой связи разработка новых пластификаторов для композиций ПВХ-материалов отделочного назначения является актуальной и практически значимой задачей. В настоящей работе приведены исследований методов получения и физико-химические свойства оксиалкилированных спиртов (бутанол, 2-этилгексанол и фенол) и фталатов на их основе, а также результаты испытаний фталатов оксиалкилированных спиртов в качестве пластификаторов ПВХ в рецептуре верхнего слоя линолеума. Отмечено, что полимерные композиции обладают более высокими значениями текучести расплава. Как показали проведенные исследования, ПВХ-рецептуры верхнего слоя линолеума с добавлением разработанных нами пластификаторов, по всем показателям удовлетворяют требованиям действующих стандартов, а при использовании бутоксиалкилфеноксилфталатов по таким показателям, как бензостойкость, % (1,25-1,53) и маслостойкость, % (10,2-10,8) даже превосходят стандартные образцы. Разработанные фталаты на основе оксиалкилированных спиртов представляются перспективными пластификаторами поливинилхлорида.

Key words: 2-ethylhexanol, petrol-resistance, butanol, butoxyethanol, butoxyethylphenoxyethylphthalate, dibutyl phthalate,

dioctyl phthalate, oil resistance, oxyalkylations, alkoxyated alcohols based phthalates, elongation at rupture, melt flow index, tensile strength, PVC linoleum, PVC compounding, PVC plasticizers, thermal stability.

Ключевые слова: 2-этилгексанол, бензостойкость, бутанол, бутоксиэтанол, бутолксиэтилфеноксиэтилфталаты, дибутилфталат, диоктилфталат, маслостойкость, оксиалкилирование, фталаты оксиалкилированных спиртов, относительное удлинение при разрыве, показатель текучести расплава (ПТР), прочность при растяжении, ПВХ-линолеум, ПВХ-рецептура, пластификаторы ПВХ, термостабильность.

Polyvinyl chloride (PVC), along with such polymers as polyethylene, polypropylene and polystyrene, refers to the number of basic chemical products, because of long working life, strength in sub-zero and at above zero temperatures, resistance to acids and alkalis, lower inflammability compared to other polymers and easily accepts any form, as well as the feedstock for the production of many kinds of products for industrial and domestic purposes. The widest range of application of polymeric materials is building trade. Most of it goes to the hard profiled moldings: window and door frames, siding, vinyl siding, moldings, linings, fillers and stuff. Plasticized PVC (plasticate) is one of the main components for the preparation of materials and products for different purposes with a wide range of operational and mechanical characteristics. Above all, building finishing materials, such as linoleum, vinyl, wallpaper, as well as materials for cables, insulation, hoses, gaskets, transparencies, decorative oilcloth and others [1-4].

High growth rates of construction, as well as finishing and repair work to date provides great potential for the development of floor coverings market. The estimated volume of Russian-made flooring is about 260-300 million m², where the share of linoleum accounts for about 35-45 % . Currently, over 80 % of the total produced in the world linoleum falls on the share of PVC coatings [1,5,6].

In order to create materials with desired properties the base polymers are mixed with other substances. Typically, modern polymer materials are multicomponent systems, which in addition to the polymer backbone are present various additives. The content of additives in the polymer composition may vary within very wide limits. Depending on the task, the type and nature of the polymer additives, it can range from one percent to 95 % [1,2,7].

In the manufacture of PVC linoleum binders, plasticizers, diluents, fillers, and dyes are applied. The concrete structure of composition may vary within wide limits depending on the type and purpose of the material. PVC characterized thermoplasticity and linear macromolecular structure are used as the binder. Natural drying oil, oksol, chloroparaffin and mineral oil (spindle and transformer) are used diluents. Talc, barite (barytes), chalk, asbestos fiber, wood flour are usually used the fillers. As a fabric base for PVC linoleum kordel and jute fabric are used. For painting linoleum in various colors used earth pigment (ocher, red ochre and red iron oxide) and minerals (white lead and titanium dioxide, lithopone, milori blue, ultramarine, chrome greens, multiple crowns, etc.) pigments. Calcium stearate, lead, lead silicate (in very small quantities) are compounded in the linoleum composition is as stabilizers. For simplification of some processing of linoleum weight (for example, rollings) stearin, rosin and other additives in very insignificant quantities added.

Irrespective of basis existence linoleum can consist of several polymeric layers. Top - a front layer of linoleum produce with the minimum quantity of fillers or at all without them that gives it the increased abrasion resistance. The consumption of dyes also decreases as only top thin layer of linoleum weight is painted over. Thickness of the top layer, as a rule, makes 17-25 % of thickness of all linoleum. The top layer is finished especially carefully. The modern equipment allows to trim front layer as a marbled and other stones with beautiful decorative properties. The subsequent layer more rigid, contains less polymeric binding [5,8-10].

To make the articles flexibility and for simplification of processing of PVC it is normally plasticized, wherein the plasticizer content is up to 40 %.

The most commonly used plasticizers are dioctyl phthalate and dibutyl phthalate. Dioctyl phthalate is considered an international standard PVC plasticizer meeting the requirements of processing, but it is relatively expensive and deficient. Therefore, dibutyl phthalate is widespread as a part of linoleum PVC compounding due to the low cost, but it does not provide long-term performance of PVC compounds. Dibutyl phthalate has a high volatility. This leads to intense loss of plasticizer from plastic compound, as well as significant deterioration of physicochemical and operational properties of the products received on its basis.

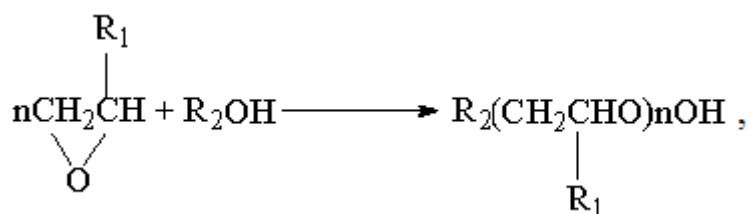
At plasticization of polyvinylchloride and its copolymers it is applied butyl benzyl phthalate is used. It possesses high plasticizing properties and is known as plasticizer of suspension and emulsion PVC, polyvinyl butyral rubbers and chlorinated rubber. Butyl benzyl phthalate is applied in production of engineering plastics, artificial leather and other petrol-resistant, oil-resistant PVC materials. However, due to the scarcity of benzyl alcohol its issue is limited [11-18].

Therefore expansion of the range of the plasticizers improving physicomechanical and operational properties of compoundings of polyvinylchloride compositions, used for receiving construction and finishing materials and products, is relevant and practically significant task.

In order to implement this direction we synthesized phthalates based alkoxyated butanol 2- ethylhexanol and phenol (oxyalkylation degree varies from 1,0 to 3,5).

One of the ways to engage butanol, 2-ethylhexanol and phenol in the synthesis is to obtain effective plasticizers phthalates oxyalkylated alcohols. The oxyalkylation of alcohols carried out by conventional methods.

Oxyalkylation reaction of alcohols is well studied and implemented on an industrial scale [17, 19]. The process is conducted at temperatures of 110-180 °C by passing through a heated alcohol ethylene oxide (propylene). Sodium hydroxide or potassium hydroxide mostly used as the catalyst [20]. Exit of products of oxyalkylation is quantitative.



- where
- $\text{R}_1 = \text{H}, \quad \text{R}_2 = \text{C}_4\text{H}_9 \quad (\text{compound } \text{№} 1-5);$
 - $\text{R}_1 = \text{H}, \quad \text{R}_2 = \text{C}_8\text{H}_{17} \quad (\text{compound } \text{№} 6-10);$
 - $\text{R}_1 = \text{H}, \quad \text{R}_2 = \text{C}_6\text{H}_5 \quad (\text{compound } \text{№} 11-15);$
 - $\text{R}_1 = \text{CH}_3, \quad \text{R}_2 = \text{C}_4\text{H}_9 \quad (\text{compound } \text{№} 16-20);$
 - $\text{R}_1 = \text{CH}_3, \quad \text{R}_2 = \text{C}_8\text{H}_{17} \quad (\text{compound } \text{№} 21-25);$
 - $\text{R}_1 = \text{CH}_3, \quad \text{R}_2 = \text{C}_6\text{H}_5 \quad (\text{compound } \text{№} 26-30).$

We have obtained several fractions and analyzed ethoxylated alcohols with a degree of ethoxylation of from 1,0 to 3,0 and propoxylated alcohols with a degree of 1,3 to 3,5 oxypropylation. Alkoxyated alcohols are colorless transparent liquid, readily soluble in water.

Their physicochemical properties are shown in tables 1, 2.

The obtained alkoxyated alcohols were subsequently used for synthesis phthalates of ethoxylated and propoxylated alcohols.

One of the most common PVC plasticizers is nonsymmetrical phthalate. For example, phthalic acid esters such as butyl benzyl phthalate and butyl 2-ethylhexyl phthalate, widely used for obtaining products of polyvinyl chloride, such as linoleum, upholstery and pressure-cast footwear [21].

Nonsymmetrical phthalic acid esters that contain side chains of different alkyl groups, are characterized by good plasticising properties and a sufficiently low volatility. Moreover, nonsymmetrical ethers gives the composition a number of other specific properties.

It is known that with increasing the rate of esterification of phthalic anhydride with alcohols their molecular weight decreases [22]. In this connection, for the synthesis of nonsymmetrical phthalates (1, 2) method of sequential esterification of phthalic anhydride to form the maximum numbers of nonsymmetrical esters were used [23].

Based on the premise that the anhydride group reacts with alcohols faster and easier than the carboxyl group, it can be said that in the reaction of phthalic anhydride with alkoxyated alcohols only monoesters are formed.

The monoester was obtained at a temperature of 110-140 °C, used as the catalyst para-toluene sulphonic acid. The depth of the esterification was monitored by the amount of evolved water and esterifier acid number.

Then, without isolating the phthalic acid monoester esterification with 25-50 % excess of the corresponding alcohol (butanol or 2-ethylhexanol) (1) or alkoxyated alcohol (butanol) was performed in the preparation butoxylalkylphenoxyalkylphthalate (2) at the reflux temperature of the reaction mass. To facilitate removal of water xylene solvent was used and the reaction mixture was sparged with an inert gas.

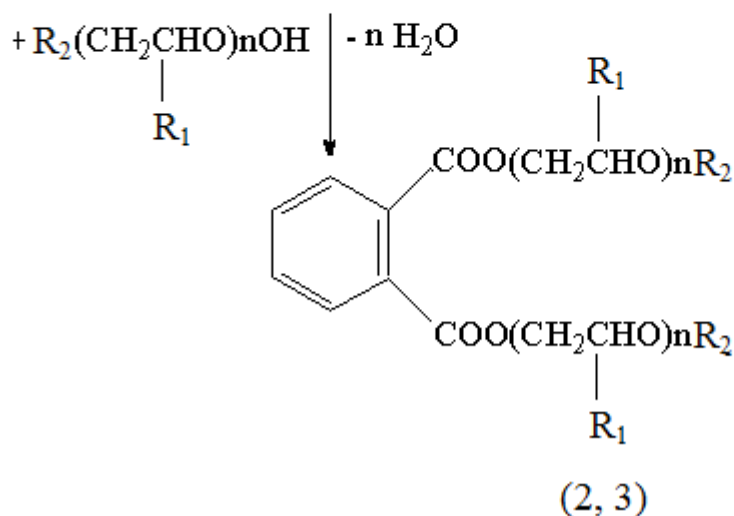
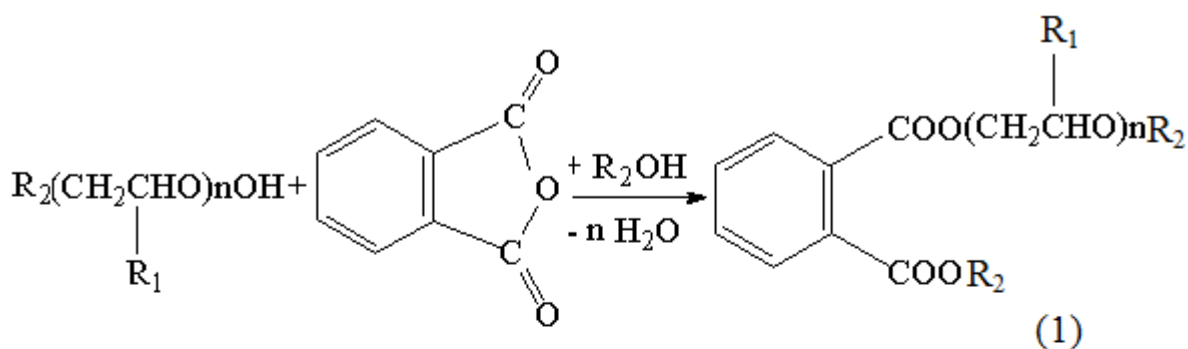
Esterification of phthalic anhydride by fatty alcohols was investigated in a number of papers [24-28]. It is shown that the esterification proceeds in two stages. Monoalkilftalat is formed as an intermediate product. The first stage is completed very quickly: the reaction rate of the first stage of esterification of phthalic anhydride is almost 100 times larger than of the second [29]. After dissolution of phthalic anhydride (at temperatures above 100 °C) virtually complete conversion of phthalic anhydride to monoalkilftalat is observed.

According to our experiments at 100-130 °C in the esterification of phthalic anhydride by oxyalkylated alcohols in 40 minutes in the reaction mixture does not detect unreacted phthalic anhydride. With further maintaining the reaction mixture at these temperatures begins to form diesters, which is evidenced by isolation of water. Therefore, finding the optimal conditions for the esterification of phthalic anhydride was reduced to study only the second reaction step.

The reaction was carried out by the conventional method of phthalic anhydride esterification by oxyalkylated alcohols (butanol or 2-ethylhexanol) in the presence of para-toluene sulphonic acid with symmetrical oxyalkylated alcohols phthalates formation (3). When the molar ratio of initial reagent s phthalic anhydride: oxyalkylated alcohol 1:2,5 (25 % molar excess of the alcohol component) diester was

synthesized in the presence of para-toluene sulphonic acid at amount of 1-2 % (by weight on the load) at 120-180 °C.

After beginning of the reaction in a certain periods of time esterifier samples were taken and analyzed for esters. The start of the reaction of water allocation was taken as the beginning of the reaction. To facilitate removal of formed water the reaction mixture was sparged with an inert gas - nitrogen or carbon dioxide.



- where (1) $\text{R}_1 = \text{H}, \quad \text{R}_2 = \text{C}_4\text{H}_9, \text{R}_2 = \text{C}_4\text{H}_9$ (compound № 31-34);
 $\text{R}_1 = \text{H}, \quad \text{R}_2 = \text{C}_8\text{H}_{17}, \text{R}_2 = \text{C}_8\text{H}_{17}$ (compound № 35-38);
 $\text{R}_1 = \text{CH}_3, \quad \text{R}_2 = \text{C}_4\text{H}_9, \text{R}_2 = \text{C}_4\text{H}_9$ (compound № 44-47);
 $\text{R}_1 = \text{CH}_3, \quad \text{R}_2 = \text{C}_8\text{H}_{17}, \text{R}_2 = \text{C}_8\text{H}_{17}$ (compound № 48-51);
(2) $\text{R}_1 = \text{H}, \quad \text{R}_2 = \text{C}_6\text{H}_5, \text{R}_2 = \text{C}_4\text{H}_9$ (compound № 39-43);

- $R_1 = \text{CH}_3, R_2 = \text{C}_6\text{H}_5, R_2 = \text{C}_4\text{H}_9$ (compound № 52-56);
 (3) $R_1 = \text{H}, R_2 = \text{C}_4\text{H}_9, R_2 = \text{C}_4\text{H}_9$ (compound № 57-60);
 $R_1 = \text{H}, R_2 = \text{C}_8\text{H}_{17}, R_2 = \text{C}_8\text{H}_{17}$ (compound № 61-64);
 $R_1 = \text{CH}_3, R_2 = \text{C}_4\text{H}_9, R_2 = \text{C}_4\text{H}_9$ (compound № 65-68);
 $R_1 = \text{CH}_3, R_2 = \text{C}_8\text{H}_{17}, R_2 = \text{C}_8\text{H}_{17}$ (compound № 69-72).

Target esters obtained with a yield higher than 80 %.

Their physicochemical properties are shown in tables 3-6. Nonsymmetrical and symmetrical phthalates alkoxyated alcohols are clear, slightly hygroscopic yellowish oily liquid, readily soluble in organic solvents, but insoluble in water [30-35].

Table 1. Physicochemical properties of ethoxylated alcohols

Indicators	Ethoxylated butanol C ₄ H ₉ (O CH ₂ CH ₂) _n OH					Ethoxylated 2-ethylhexanol C ₈ H ₁₇ (OCH ₂ CH ₂) _n OH					Ethoxylated phenol C ₆ H ₅ (OCH ₂ CH ₂) _n OH				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Compound №	1,5	2,0	2,2	2,4	3,0	1,5	2,0	2,2	2,4	3,0	1,0	1,3	1,9	2,4	2,9
Oxyethylation ratio, n															
Density, d ₄ ²⁰	0,974 5	0,984 2	0,987 5	0,989 5	1,003 3	0,914 1	0,924 0	0,927 8	0,930 9	0,938 2	1,100 7	1,104 8	1,111 1	1,115 8	1,119 7
Refraction index, n _D ²⁰	1,428 5	1,433 3	1,435 1	1,436 9	1,442 8	1,432 5	1,449 0	1,453 8	1,458 0	1,469 6	1,531 4	1,536 0	1,543 4	1,550 1	1,559 4
Essential number	790	681	644	615	533	568	510	488	471	422	789	723	619	552	497
Molecular mass, found	142	165	173	182	210	197	220	230	238	265	142	155	181	203	225
Molecular mass, calculated	140	162	171	180	206	196	218	227	236	262	138	151	178	200	222

Table 2. Physicochemical properties of oxypropylated alcohols

Indicators	Oxypropylated butanol C ₄ H ₉ (CH ₃ CHOCH ₂) _n OH					Oxypropylated 2-ethylhexanol C ₈ H ₁₇ (CH ₃ CHOCH ₂) _n OH					Oxypropylated phenol C ₆ H ₅ (CH ₃ CHOCH ₂) _n OH				
	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Compound №	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Oxypropylation ratio, n	1,5	2,0	2,2	2,4	3,2	1,5	2,0	2,2	2,4	3,2	1,3	1,6	2,1	2,8	3,5
Density, d ₄ ²⁰	0,913 0	0,922 4	0,925 3	0,928 7	0,942 9	0,874 7	0,879 2	0,881 7	0,884 8	0,893 8	1,064 7	1,070 2	1,077 3	1,084 6	1,090 1
Refraction index, n _D ²⁰	1,427 4	1,428 9	1,429 6	1,430 3	1,433 3	1,433 3	1,434 9	1,435 5	1,436 1	1,438 4	1,524 4	1,528 8	1,533 8	1,538 7	1,542 3
Essential number	693	586	552	522	428	512	451	429	410	351	655	589	514	432	372
Molecular mass, found	162	192	203	215	262	219	248	261	273	319	171	190	218	259	301
Molecular mass, calculated	161	190	202	213	260	217	246	258	270	316	169	187	216	256	297

Table 3. Physicochemical properties of nonsymmetrical phthalates of ethoxylated alcohols

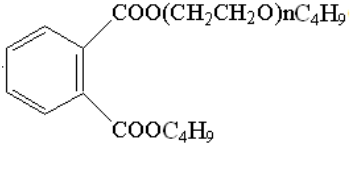
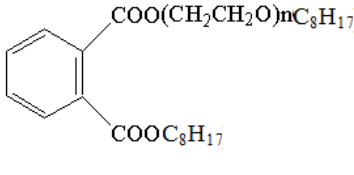
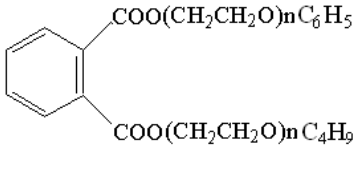
Indicators					Dibutyl phthalate					Dioctyl phthalate						Dibutyl phthalate
	31	32	33	34		0,0	33	34	35		36	0,0	39	40	41	
Compound №	31	32	33	34	0,0	33	34	35	36	0,0	39	40	41	42	43	0,0
Oxyethylation ratio, n	1,4	2,0	2,5	2,9	0,0	1,5	2,0	2,4	3,0	0,0	1,0	1,4	1,7	2,0	2,5	0,0
Density, d_4^{20}	1,4890	1,4883	1,4876	1,4870	1,4904	1,4812	1,4790	1,4768	1,4748	1,4871	1,5190	1,5183	1,5180	1,5176	1,5170	1,4904
Refraction index, n_D^{20}	1,0554	1,0581	1,0619	1,0645	1,0432	0,9875	0,9930	0,9986	1,0097	0,9750	1,1054	1,1081	1,1110	1,1119	1,1145	1,0432
Acid number	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,2	0,2	0,2	0,2	0,2	0,1
Essential number	325	302	285	272	401	242	231	222	213	287	293	272	261	251	237	401
Molecular mass, found	345	371	393	412	279	463	485	505	526	397	391	412	429	446	473	279
Molecular mass, calculated	340	366	388	406	278	456	478	496	522	390	386	404	417	430	452	278
Solidification point, °C	-50	-50	-50	-48	-40	-54	-54	-52	-52	-60	-39	-40	-40	-40	-39	-40
Volatiles mass fraction (100 °C, 6 hrs.), %	0,20	0,28	0,20	0,20	0,30	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,30
Flash-point, °C	197	197	199	199	168	200	214	200	200	205	200	200	200	200	200	168

Table 4. Physicochemical properties of nonsymmetrical phthalates of oxypropylated alcohols

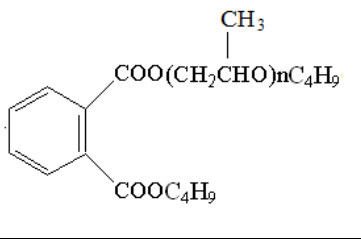
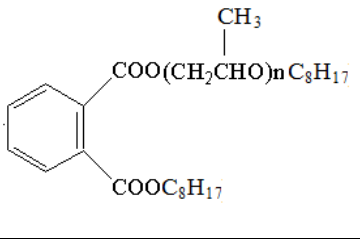
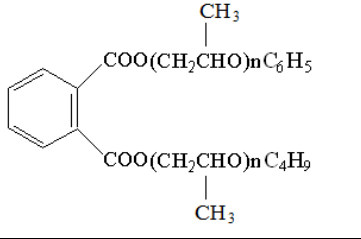
Indicators					Dibutyl phthalate					Dioctyl phthalate						Dibutyl phthalate
	44	45	46	47		48	49	50	51		52	53	54	55	56	
Compound №	44	45	46	47	0,0	48	49	50	51	0,0	52	53	54	55	56	0,0
Oxypropylation ratio, n	1,7	2,2	2,8	3,5	0,0	1,3	1,9	2,3	2,7	0,0	1,1	1,5	1,8	2,2	2,6	0,0
Density, d ₄ ²⁰	1,480 6	1,478 1	1,476 5	1,475 3	1,4904	1,477 5	1,474 5	1,473 3	1,471 9	1,4871	1,51 83	1,51 79	1,51 74	1,51 70	1,516 5	1,4904
Refraction index, n _D ²⁰	1,025 3	1,030 7	1,037 5	1,041 4	1,0432	0,968 1	0,973 8	0,977 6	0,981 3	0,9750	1,10 04	1,10 32	1,10 50	1,10 64	1,107 9	1,0432
Acid number	0,03	0,08	0,10	0,20	0,10	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,1
Essential number	293	272	251	227	401	237	220	210	201	287	262	249	239	228	218	401
Molecular mass, found	382	412	446	493	279	473	509	533	557	397	427	450	468	492	514	279
Molecular mass, calculated	377	406	440	481	278	465	500	523	547	390	421	444	461	485	508	278
Solidification point, °C	-58	-52	-51	-50	-40	-50	-50	-50	-47	-60	-35	-38	-37	-37	-36	-40
Volatiles mass fraction (100 °C, 6 hrs.), %	0,43	0,20	0,40	0,20	0,30	0,100	0,120	0,112	0,100	0,100	0,10	0,12	0,10	0,10	0,10	0,30
Flash-point, °C	200	197	197	199	168	200	206	200	200	205	200	200	200	200	200	168

Table 5. Physicochemical properties of symmetrical phthalates of ethoxylated alcohols

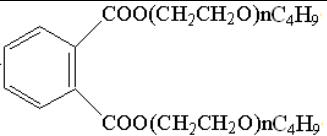
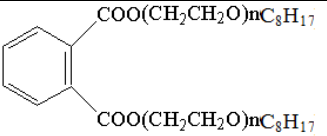
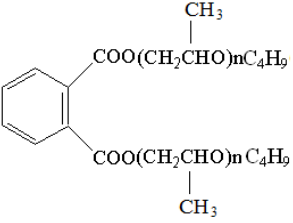
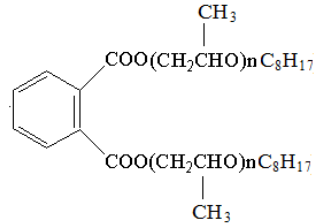
Indicators					Dibutyl phthalate					Dioctyl phthalate
	57	58	59	60		61	62	63	64	
Compound №	57	58	59	60	0,0	61	62	63	64	0,0
Oxyethylation ratio, n	1,4	2,0	2,5	2,9	0,0	1,5	2,0	2,4	3,0	0,0
Density, d_4^{20}	1,4857	1,4816	1,4775	1,4761	0,0	1,4797	1,4783	1,4772	1,4754	1,4871
Refraction index, n_D^{20}	1,0647	1,0757	1,0827	1,0883	1,4904	0,9887	0,9982	1,0047	1,0132	0,9750
Acid number	0,2	0,1	0,3	0,3	1,0432	0,30	0,30	0,38	0,30	0,10
Essential number	275	243	221	206	0,1	211	195	183	168	282
Molecular mass, found	407	461	507	544	401	531	574	612	667	397
Molecular mass, calculated	401	454	498	533	279	522	566	601	654	390
Solidification point, °C	-50	-50	-49	-47	278	-57	-55	-54	-50	-60
Volatiles mass fraction (100 °C, 6 hrs.), %	0,20	0,25	0,25	0,20	-40	0,1	0,1	0,1	0,1	0,1
Flash-point, °C	200	200	200	199	0,30	200	200	200	200	205

Table 6. Physicochemical properties of symmetrical phthalates of oxypropylated alcohols

Indicators					Dibutyl phthalate					Diethyl phthalate
	65	66	67	68		69	70	71	72	
Compound №	65	66	67	68	0,0	69	70	71	72	0,0
Oxypropylation ratio, n	1,7	2,2	2,8	3,5	0,0	1,3	1,9	2,3	2,7	0,0
Density, d_4^{20}	1,4771	1,4745	1,4710	1,4683	1,4904	1,4619	1,4607	1,4599	1,4594	1,4871
Refraction index, n_D^{20}	1,02865	1,02991	1,03100	1,03180	1,04320	0,9642	0,9978	1,0253	1,0429	0,9750
Acid number	0,3	0,4	0,3	0,3	0,1	0,3	0,4	0,3	0,5	0,1
Essential number	232	207	182	160	401	203	180	166	155	282
Molecular mass, found	483	541	615	700	279	552	622	675	722	397
Molecular mass, calculated	475	533	603	684	278	541	610	657	703	390
Solidification point, °C	-46	-44	-42	-40	-40	-49	-47	-43	-43	-60
Volatiles mass fraction (100 °C, 6 hrs.), %	-	0,25	0,35	0,50	0,30	0,07	0,12	0,10	0,10	0,10
Flash-point, °C	Higher 200	Higher 200	Higher 200	Higher 200	168	200	200	200	200	205

As showed the conducted researches, the obtained phthalates of oxyalkylated butanol and butoxylalkylphenoxyalkylphthalates are less volatile compounds than commercially available plasticizer dibutyl phthalate, obtained phthalates of oxyalkylated 2- ethylhexanol by the volatility degree corresponds to dioctyl phthalate. From other indicators derived plasticizers also correspond to the level of dioctyl phthalate. Physicochemical parameters of obtained plasticizers analyzed according to GOST 8728-88.

Choosing plasticized composition for a particular product is determined by its operating conditions. Selection criteria are varied and depend on the destination of the product. One of the main characteristics of the polymeric material of criteria are its physical, mechanical and rheological properties: strength and elongation at break, the melt flow rate, petrol and oil extractability [1, 7, 8].

Taking into account the results of the determination of physicochemical and physicomechanical properties alkoxyated alcohols phthalates prototypes were tested as plasticisers in PVC [32,36-38]. From the obtained compounds nine samples were tested as plasticizers in PVC compounding linoleum upper layer. Prototypes of plasticizers were added in PVC instead of commercially available analog - dioctyl phthalate (prototype I - compound number 64; prototype II - compound number 72; prototype V - compound number 66; prototype III - compound number 35; prototype IV - compound number 51; prototype VI – compound number 47; prototype VII – compound number 39; prototype compound VIII – compound number 42; prototype IX – compound number 43; number prototype X – compound number 52). Results of obtained plasticizers testing are shown in Table 7.

Table 7. Results of tests developed plasticizers in the formulation of industrial top layer of linoleum (plasticized PVC compound with transparent textured surface and without embossing)

Indicator name	STP standards 00203312-100- 2006	PVC plastic with the proposed plasticizers									
		I	II	III	IV	V	VI	VII	VIII	IX	X
Tensile strength, kgf/cm ² along	Not less										
	175	279	294	285	290	284	287	285	273	269	272
across	175	241	221	254	227	258	232	249	225	237	240
Elongation at break,% along	Not less										
	100	297	318	249	263	249	275	260	283	267	254
across	100	253	301	266	253	258	269	241	261	254	225
Change in linear dimensions,%	Not more 3	2	1,3	1,7	1,8	1,2	1,4	2,4	2,2	1,9	2,6
Production data											
Thermal stability at 180 °C, minutes	With dioctyl phthalate 1h 45 minutes	1h 35 minutes	1h 48 minutes	1h 40 minutes	1h 37 minutes	1h 51 minutes	1h 43 minutes	1h 48 minutes	1h 33 minutes	1h 54 minutes	1h 43 minutes
Melt flow index, g/10 min T = 170 °C, P = 16,6 kG	7,1	7,5	8,3	9,1	8,9	9,3	8,6	8,0	7,5	8,2	7,1

As shown by researches, PVC formulations of the upper layer of linoleum with the addition of our developed plasticizers, by all indicators meet the requirements of existing standards, while using butoxylalkylphenoxyalkylphthalates superior to standard samples in petrol and oil resistance. Thus, for compounds № 39, 42, 43, 52 petrol resistance varies from 1,26 % to 1,53 %; oil resistance ranges from 10,2 % to 10,8 %.

Conclusions

Thus, the results of testing synthesized oxyalkylated alcohols phthalates have a relatively high efficiency as PVC plasticiser and recommended for use in PVC compounding the aforementioned top layer linoleum.

References

1. Polyvinylchloride / Wilkie Ch. [and other]. SPb.: Professija, 2007. pp 728.
2. Polymers in construction / Malbiev S.A. [and other]. Moscow: Vicshay Shkola, 2008. pp 456.
3. Vinyl chloride copolymers release // Bulletin of the chemical industry, 2012. № 4 (67). P. 39 -44.
4. Polyvinyl chloride / Ulyanov V.M. [and other]. Moscow: Khimiya, 1992. pp 288.
5. Rybev I.A. Construction materials. Textbook manual for building university specialties. 2nd publ., cor. Moscow: Vicshay Shkola, 2004. pp 701.
6. Building materials (Materials science. Building Materials) / Mikulski V.G. [and other]. M.: ASB, 2004. pp 536.

7. Manufacture of polymeric materials / Kryzhanovsky V.K. [and other]. St. Petersburg: Professiya, 2004. pp 464.
8. The general course of construction materials: Textbook manual for building university specialties / Rybev I.A. [and other]. Moscow: Vicshay Shkola, 1987. pp 584.
9. Domokeev A.G. Building Materials. Moscow: Vicshay Shkola, 1988. pp 236 .
10. Building materials and products / Popov K.N. [and other]. Moscow: Vicshay Shkola, 2006. pp 440.
11. Polymers plasticizers / Bartshteyn R.S. [and other]. Moscow: Khimiya, 1982. pp 196.
12. Polyvinyl chloride's plasticizers / Mazitova A.K. [and other]. Voronezh: VSPU, 2011. Science and epoch: monograph, Book 7. P. 276 – 296.
13. PVC linoleum with improved performance characteristic / Aminova G.K. [and other]. / Science, Technology and Higher Education: materials of the II international research and practice conference. Canada, 2013. Vol. II. 16-19.
14. PVC linoleum / Aminova G.K. [and other]. Voronezh: VGPU, 2013. Science and epoch: monograph, Book 11. P. 187-212.
15. Maskova A.R. Polyvinyl chlorides composition for building purpose plasticized by phthalates of oxyalkylated alcohols: candidate's dissertation: Ufa, 2012. pp. 143.
16. Plasticizing of polyvinyl chloride with esters of alkosinaphtenic acid / Mamedoov R.I. [and other] // Plast. massy, 1972. № 10. P. 39-40.
17. Hamaev V.H. Synthesis and investigation of properties of ester's compound and development of plasticizers and additives for synthetic oils: Ph.D. dissertation, Ufa, 1982. pp 486.

18. Certificate of authorship 938533 (USSR). Butylphenoxyphthalate in the quality of polyvinyl chloride's plasticizer. Hamaev V.H., Bikkulov A.Z., Mazitova A.K., Hannanov R.N., Svinuhov A.G., Smorodin A.A., Pavlychev V.N., Teplov B.F.

19. Shvets V.F. Kinetics and mechanism of the alpha-oxides: Author's abstract doctor of Science thesis, M., 1974. pp. 53.

20. Schoenfeld N. Nonionic detergents. Moscow: Khimiya, 1965. pp 488.

21. Report relating 61.9.33.02 "Development of technology for new plasticizers SGS C₅-C₆". UPI. 1979. P. 129.

22. The esterification of phthalic anhydride by higher alcohols in the presence of titanium catalysts / Bolotina L.M. [and other] // *Plastics*, 1973. № 7. P.13 -15.

23. Application of higher alcohols of different fractional composition for the nonsymmetrical phthalate plasticizer synthesis / Ignatova G.N. [and other] // *Chem. prom.*, 1971. № 1. P.14 - 17.

24. Synthesis and investigation of alkoxyated alcohols phthalates / Grigoriev V.B. [and other] // "Chemicals, Petrochemicals and Refining: Abstracts and reports of Scientific and Technical Conference". Ufa Petroleum Institute. Ufa, 1982. pp. 56.

25. Preparation of dibutyl phthalate and dibutyl sebacate in the presence tetrabutoxytitanium / Bolotina L.M. [and other] // *Plastics*, 1978. № 8. pp. 580 -582 .

26. Some kinetic regularities of esterification of phthalic anhydride by 2-ethylhexanol in the presence of acid catalysts /Nosovskii Y.E. [and other] // *Khim.prom.* 1974 . № 2. P.108- 111.

27. Emmet E. Esterification // *Industr. Eng. Chem.*, 1954. Vol. 46. P.1801 -1809.

28. Industrial method of obtaining nonsymmetrical phthalates / Bolotina L.M. [and other] // Chem. prom., 1978. № 4. P. 257-259.

29. Symmetrical and nonsymmetrical phthalates as PVC plasticizers / Aminova G.K. [and other] // Bashkir Chemistry Journal 2011. T.18. № 3. P. 175-176 .

30. Symmetrical and nonsymmetrical alkoxyated alcohols phthalates / Aminova G.K. [and other] // Bashkir Chemistry Journal, 2011. Vol. 18. № 1. P. 147-151.

31. New types of composite PVC finishing materials / Aminova G.F. [and other] // News of the Kazan State Architectural University, 2013. 3 (25). P. 80-85.

32. Synthesis of butoxyethylphenoxyethylphthalate / Aminova G.F. [and other] / 64th Scientific Conference of Students and Young Scientists: collection of conference material / Editorial Board. Ufa: Izd UGNTU, 2013. Book 2. P. 261-263 .

33. Synthesis and potential applications of symmetric phthalates of oxypropylated butanol /Aminova G.K. [and other]. / Actual problems of engineering, natural sciences and humanities: Proceedings of the International Scientific and Technical Conference. Ufa: IE Verko “Pечатnij dom”, 2013. Issue. 7. P. 9-11.

34. Synthesis and properties of octylalkoxy phthalates / Buylova E.A. [and other] / Actual problems of engineering, natural sciences and humanities: Proceedings of the International Scientific and Technical Conference. Ufa: IE Verko “Pечатnij dom”, 2013. Issue. 7. P. 47 -49.

35. Plasticizers for polyvinyl chloride compositions for building purpose /Aminova G.K. [and other] // Industrial production and use elastomers, 2012. № 4. P. 29-32.

36. PVC formulations testing for construction application using symmetrical and nonsymmetrical alkoxyated alcohols phthalates / Maskova A.R. [and other] // News of the Kazan State Architectural University, 2012. № 2 (20). P. 177-182.

37. Investigation of plasticizing properties of symmetric oxypropylated alcohols phthalates in PVC formulations multilayer baseless linoleum / Maskova A.R. [and other] / Proceedings of the XVI Intern. Scientific-Technical. conf. / Editorial Board. Ufa: USPTU, 2012. Vol.2. P. 197-198.

38. Alkoxyated alcohols phthalates - PVC compounds plasticizers for construction purposes / Aminova G.K. [and other] // Bashkir Chemistry Journal, 2012. Vol.19. № 3. P.118-121.

Литература

1. Поливинилхлорид / Уилки Ч. [и др.]. СПб.: Профессия, 2007. 728 с.
2. Полимеры в строительстве / Малбиев С.А. [и др.]. М.: Высшая школа, 2008. 456 с.
3. Выпуск винилхлорида и сополимеров // Вестник химической промышленности, 2012. № 4 (67). С.39-44.
4. Поливинилхлорид /Ульянов В.М. [и др.]. М.: Химия, 1992. 288 с.
5. Рыбьев И.А. Строительное материаловедение Учеб. пособие для строит. спец. вузов. 2-е изд., испр. М.: Высшая школа, 2004. 701 с.
6. Строительные материалы (Материаловедение. Строительные материалы) / Микульский В.Г. [и др.]. М.: АСВ, 2004. 536 с.

7. Производство изделий из полимерных материалов / Крыжановский В.К. [и др.]. СПб.: Профессия, 2004. 464 с.
8. Общий курс строительных материалов: Учеб. пособие для строит. спец. вузов / Рыбьев И.А. [и др.]. М.: Высшая школа, 1987. 584 с.
9. Домокеев А.Г. Строительные материалы. М.: Высшая школа, 1988. 236 с.
10. Строительные материалы и изделия / Попов К.Н. [и др.]. М.: Высшая школа, 2006. 440 с.
11. Пластификаторы для полимеров / Бартштейн Р.С. [и др.]. М.: Химия, 1982. 196 с.
12. Пластификаторы поливинилхлорида / Мазитова А.К. [и др.]. Воронеж: ВГПУ, 2011. Наука и эпоха: монография, кн. 7. С. 276-296.
13. PVC linoleum with improved performance characteristic / Aminova G.K. [and other] / Science, Technology and Higher Education: materials of the II international research and practice conference. Canada, 2013. Vol. II. P. 16-19.
14. Поливинилхлоридные линолеумы / Аминова Г.К. [и др.]. Воронеж: ВГПУ, 2013. Наука и эпоха: монография, кн. 11. С. 187-212.
15. Маскова А.Р. Поливинилхлоридные композиции строительного назначения, пластифицированные фталатами оксиалкилированных спиртов: дис....канд. техн. наук. Уфа, 2012. 143 с.
16. Пластификация поливинилхлорида сложными эфирами алкосинафтенных кислот / Мамедов Р.И. [и др.] // Пласт. массы, 1972. № 10. С. 39-40.
17. Хамаев В.Х. Синтез и исследование свойств сложноэфирных соединений и разработка на их основе пластификаторов и

компонентов синтетических масел: дис....докт. тех. наук. Уфа, 1982. 486 с.

18. А.с. 938533 (СССР). Бутилфеноксиптилфталат в качестве пластификатора поливинилхлорида. Хамаев В.Х., Биккулов А.З., Мазитова А.К., Ханнанов Р.Н., Свинухов А.Г., Смородин А.А., Павлычев В.Н., Теплов Б.Ф.

19. Швец В.Ф. Кинетика и механизм реакций альфа-окисей: автореф. дис....докт. хим. наук. М., 1974. 53 с.

20. Шенфельд Н. Неионогенные моющие средства. М.: Химия, 1965. 488 с.

21. Отчет по теме 61.9.33.02 «Разработка технологии получения новых пластификаторов СЖС С₅-С₆. Уфа: УНИ, 1979. 129с.

22. Этерификация фталевого ангидрида высшими спиртами в присутствии титановых катализаторов /Болотина Л.М. [и др.] // Пласт. массы. 1973. № 7. С.13-15.

23. Использование высших спиртов различного фракционного состава для синтеза несимметричных фталатных пластификаторов /Игнатова Г.Н. [и др.] // Хим. пром-ть. 1971. № 1. С.14-17.

24. Синтез и исследование фталатов оксиалкилированных спиртов /Григорьев В.Б. [и др.] //Химия, нефтехимия и нефтепереработка: тез. докл. респ. науч.-техн. конф./ УНИ. Уфа, 1982. 56 с.

25. Получение дибутилфталата и дибутилсебацата в присутствии тетрабутоксититана /Болотина Л.М. [и др.] // Пласт. массы. 1978. № 8. С. 580-582.

26. Некоторые кинетические закономерности этерификации фталевого ангидрида 2-этилгексанолом в присутствии кислых

катализаторов / Носовский Ю.Е. [и др.] // Хим. пром-ть.1974. № 2. С.108-111.

27. Esterification / Emmet E. // Industr. Eng. Chem.,1954. Vol. 46. P.1801-1809.

28. Промышленный метод получения несимметричных фталатов /Болотина Л.М. [и др.] // Хим. пром-сть. 1978. № 4. С.257-259.

29. Симметричные и несимметричные фталаты в качестве пластификаторов поливинилхлорида /Аминова Г.К. [и др.] // Башкирский химический журнал. 2011. Т.18, № 3. С. 175-176.

30. Симметричные и несимметричные фталаты оксиалкилированных спиртов /Аминова Г.К. [и др.] // Башкирский химический журнал. 2011. Т.18, № 1. С. 147-151.

31. Новые типы композиционных ПВХ-материалов отделочного назначения / Аминова Г.Ф. [и др.] // Известия КГАСУ. 2013. 3(25). С. 80-85.

32. Синтез бутоксиэтилфеноксипропилфталатов /Аминова Г.Ф. [и др.] / Материалы 64-ой науч.-техн. конф.студентов, аспирантов и молодых ученых: сб. матер. конф. Уфа: Изд-во УГНТУ, 2013. Кн. 2. С. 261-263.

33. Синтез и возможные области применения симметричных фталатов оксипропилированного бутанола /Аминова Г.К. [и др.] / Актуальные проблемы технических, естественных и гуманитарных наук: материалы Междунар. науч.-техн. конф. Уфа: ИП Верко «Печатный домъ», 2013. Вып. 7. С.9-11.

34. Синтез и свойства октилалкоксифталатов / Буйлова Е.А. [и др.] / Актуальные проблемы технических, естественных и гуманитарных наук: материалы Междунар. науч.-техн. конф. Уфа: ИП Верко «Печатный домъ», 2013. Вып. 7. С.47-49.

35. Пластификаторы для поливинилхлоридных композиций строительного назначения /Аминова Г.К. [и др.] // Промышленное производство и использование эластомеров. 2012. № 4. С. 29-32.

36. Испытание рецептур ПВХ-материалов строительного назначения с использованием симметричных и несимметричных фталатов оксиалкилированных спиртов / Маскова А.Р. [и др.] // Известия Казанского государственного архитектурно-строительного университета. 2012. № 2(20). С. 177-182.

37. Исследование пластифицирующих свойств симметричных фталатов оксипропилированных спиртов в ПВХ-рецептурах многослойного безосновного линолеума /Маскова А.Р. [и др.] / Материалы XVI Международ. науч.-техн.. конф. Уфа: УГНТУ, 2012. Т. 2. С. 197-198.

38. Фталаты оксиалкилированных спиртов – пластификаторы ПВХ-композиций строительного назначения /Аминова Г.К. [и др.] // Башкирский химический журнал. 2012. Т.19, № 3. С. 118-121.

Сведения об авторах

Information about authors

G.F. Aminova, post graduate student, FSBEI NPE “Ufa state petroleum technological university”, Ufa, Russian Federation

Аминова Г.Ф., аспирант, ФГБОУ ВПО «Уфимский государственный нефтяной технический университет», Уфа, Российская Федерация

A.I. Gabitov, dr. of tech., professor of department “Building construction” FSBEI NPE “Ufa state petroleum technological university”, Ufa, Russian Federation

Габитов А.И., д-р техн. наук, проф. кафедры «Строительные конструкции» ФГБОУ ВПО «Уфимский государственный нефтяной технический университет», Уфа, Российская Федерация

A.R. Maskova, cand. tech. sci., associate professor of department “Applied Chemistry and Physics” FSBEI NPE “Ufa state petroleum technological university”, Ufa, Russian Federation

Маскова А.Р., канд. техн. наук, доцент кафедры «Прикладная химия и физика» ФГБОУ ВПО «Уфимский государственный нефтяной технический университет», Уфа, Российская Федерация

B.R. Khusnutdinov, associate of department “Building construction” FSBEI NPE “Ufa state petroleum technological university”, Ufa, Russian Federation

Хуснутдинов Б.Р., ассистент кафедры «Строительные конструкции» ФГБОУ ВПО «Уфимский государственный нефтяной технический университет», Уфа, Российская Федерация

L.K. Abdrakhmanova, cand. tech. sci., associate professor of department “Applied Chemistry and Physics” FSBEI NPE “Ufa state petroleum technological university”, Ufa, Russian Federation

Абдрахманова Л.К., канд. техн. наук, доцент кафедры «Прикладная химия и физика» ФГБОУ ВПО «Уфимский государственный нефтяной технический университет», Уфа, Российская Федерация

R.F. Nafikova, dr. of tech., professor of department “General chemical technology” FSBEI NPE “Ufa state petroleum technological university”, Ufa, Russian Federation

Нафикова Р.Ф., д-р техн. наук, проф. кафедры «Общая химическая технология» ФГБОУ ВПО «Уфимский государственный нефтяной технический университет», Уфа, Российская Федерация

e-mail: asunasf@mail.ru