

## Получение и исследование свойств эластомерсодержащих композиций на основе соолигомеров полиоксипропиленгликоля и 4,4'-дифенил-метандиизоционата

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Проведено исследование в целях получения высоко-адгезионного и высокоэластичного покрытия клеящей и уплотняющей композиции. Получены соолигомеры полиоксипропиленгликоля и 4,4'-дифенилметандиизоционата, изучена кинетика сополиконденсации. Установлено, что реакция уретанообразования протекает по миграционной полимеризации, основанной на присоединении к атому азота подвижных водородных атомов полиэфира. Методом ИК-спектроскопии исследована морфология синтезированных соолигомеров. Показано, что совмещение соолигомера с бутилкаучуком (сополимером изобутилена и изопрена) увеличивает эластичность системы, снимает усадку и повышает термо-, химическую стойкость. С целью получения адгезионного и высокоэластичного композиционного материала изучены смеси полиуретанового соолигомера с бутилкаучуком (БК), имеющего высокие показатели теплостойкости, эластичности, химической стойкости в агрессивных средах, атмосферо- и водостойкости. Показано, что при смешении полиуретанового сополимера с бутил каучуком происходит образование полимерной системы, макромолекулы которой, механически взаимодействуя между собой, образуют так называемые взаимопроникающие сетки. Указанная композиция также наиболее устойчива в агрессивных средах, что делает ее применение перспективным. Сравнение данных дифференциально-термического анализа соолигомера и композиции соолигомер+бутил каучук показывает, что полученная композиция термически более устойчива, чем соолигомер. В работе решена важная научно-техническая проблема повышения качества адгезионных композиций. В результате проведенного исследования разработаны рекомендации по улучшению свойств адгезионных композиций, конкурентоспособных по отношению к существующим аналогам, по рецептуре, строению, технологии получения и использования адгезионных композиций. Полученные указанным путем композиции могут быть использованы в производстве полимерных изделий для нефтяной, машиностроительной промышленности.

**Ключевые слова:** химическую стойкость, полиуретановый соолигомер, бутил каучука, полимеризация, теплостойкость.

## The receiving and research of properties elastomer of the containing compositions on the basis of sooligomer of polyoxydepropylenglycol about 4,4'-diphenylmetandusothinonats

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The study in order to obtain high adhesion and high-elastic coating adhesive and sealant compositions. Received, they polyoxydepropylenglycol and 4,4'-diphenylmethanedusothionats, kinetics of sopolicondensation. It has been established that the reaction of education migration flows tint urethane polymerization based on accession to the nitrogen Atom mobile hydrogen atoms polyester. By IR spectroscopy, we investigated the morphology of synthesized sooligomers. It is shown that combining the sooligomer with butyl rubber (copolymer of isobutylene and isoprene) increases the elasticity of the system, removes shrinkage and improves thermal and chemical resistance. For the purpose of obtaining highly adhesive and highly elastic composite material made of polyurethane sooligomers mixtures has been studied with butyl rubber (BC) with high rates of heat resistance, flexibility, chemical resistance to aggressivesurroundings, resistance and water resistance. It is shown that when mixing polyurethane copolymer with butyl rubber polymer formation occurs the system, macromolecules which mechanically interacting among themselves form a so-called grid interpenetrating. This composition is also the most resistant to an aggressive surroundings, which makes its application promising. Comparison of differential thermal analysis sooligomers and compositions sooligomer+butyl rubber, shows that the composition of thermally more stable than sooligomer. In the work solved an important scientific and technical challenge of improving the quality of adhesive compositions. The study developed recommendations for improving the properties of adhesive compositions, competitive with respect to existing analogues for recipe structure, technology access and use adhesive compositions. Received by the specified by compositions can be used in the manufacture of polymer products for the oil, engineering industries.

**Key words:** chemical resistance, polyurethane sooligomer, butyl rubber, polymerization, heat resistance

### INTRODUCTION:

Chemical and physic-mechanical properties of polyurethane in many respects are defined by variety of chemical bonds of various types in its structure, and actually represent the block of sopolymers in which chain alternation of sites of various chemical natures is carried out. These features of a chemical structure of polyurethane promote receiving on their basis of materials with a wide range of physic mechanical properties[1-14].

However products on the basis of polyurethane along with the high durability and excellent wear resistance are characterized by narrow temperature intervals of

use and rather high cost. Elimination of these shortcomings can be reached by combination of polyurethane with other polymers and, thereby, is considerable expanding the field of their application [15-24].

Receiving adhesive polymeric composition on the basis of industrial polyessential - the polyoxydepropylenglycol combined at the room temperature with 4,4'-diphenylmethanedusothionats and 5% solution of butyl rubber in toluene became an object of the real research. It is known that the structure and properties of polyurethanes can be varied within wide limits by selecting appropriate starting materials. They are among the few polymers that can be purposefully regulated by the number of cross-links, the flexibility of polymer molecules, and the nature of intermolecular interactions. Polyurethanes are obtained by reacting compounds containing isothioate groups with polyfunctional hydroxyl-containing derivatives. As isothioates, we used 4,4'-diphenylmethanedusothanete, widely used in the production of elastic polyurethanes. As the hydroxyl-containing compound, polyoxydepropylenglycol was used this served as a good hydrophobic component. Thus, polyoxydepropylenglycol determines basically the complex of physic-mechanical properties of the obtained polyurethane material.

The creation of these polyurethane materials was carried out with the aim of obtaining promising polymers that characterize a complex of valuable operational properties, namely, a high index of heat resistance, elasticity, chemical resistance in corrosive media, and water resistance. To obtain on their basis coatings, film materials used in virtually all industries.

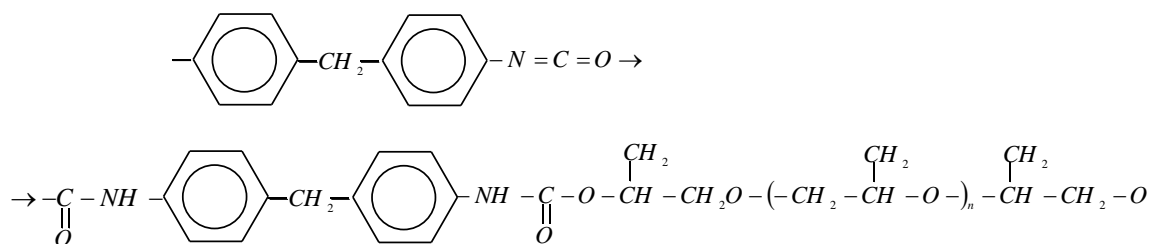
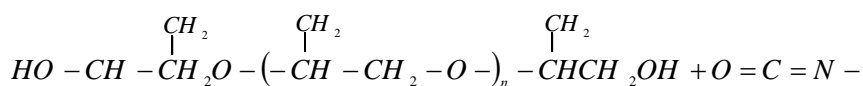
## EXPERIMENTAL METHOD

In work the following materials were used:

The industrial polyessential of Laprol brand 2502 (TU-2226-026-10488-57-98) having the following physical and chemical characteristics: acid number, mg KOH/g-0.1; molecular mass of 2500; the maintenance of OH-group, % -6.7; pH (a methanol: water -70:30) -6.1; the moisture content, %-0.1; viscosity kinematic at 30 °C, mm<sup>2</sup>/s - 540. 4,4'-difenilmetandiizotsionat (MDI), having : temperature melting T, °C-40.5;  $d_4^{50}$ -1.850;  $n_d^{50}$ -1.5906. Butyl rubber (isobutylene copolymer with an isoprene) the BK-2045 brands (TU 38003169-74): viscosity according to Mooney at 100 °C, 8 min. -45 ±4; not limitation -2 ±0.2% mol.;  $\rho$  kg/m<sup>3</sup>-865.

Combination of polyoxydepropylenglycol (PUR) with 4,4'-diphenylmethanedusothionates was carried out by mixture at the room temperature.

Mixture of polyglycols with hardeners of isothionat type reaction of urethane of education proceeds on the mechanism of migration polymerization based on ability of accession to atom of nitrogen of mobile hydrogen atom of polyessential.



From experimental results it is revealed that process of interaction of components of mix is followed by increase in viscosity with increase in concentration 4,4'-diphenylmethanedisothionats table 1.

Table 1

Contents influence the isothionats of groups on viscosity of reactionary mix  
Таблица 1. Влияние содержания изоционатных групп на вязкость реакционной смеси

Indicator	Time of interaction, minutes	Molecular mass of mix, $\bar{M}_n$	Dynamic viscosity, Pa·sec.
Maintenance of DMDIT, %:			
30	60	800	20.0
20	60	500	15.0
15	60	300	13.0

It is shown that in 60 min quantity the izotsionats of groups decreases to zero that proves course of chemical interaction for the account the izotsionats of groups. Process of a sopolikondensation comes to the end at their full expenditure. The viscosity of reactionary weight increases also with increase in time of a sopolikondensation from 0 to 60 min, and time of full expenditure the izotsionats of groups coincides with a point of the maximum viscosity of a sooligomer.

Extraction of a hinge plate of a sooligomer acetone in the device Soksleta has defined extent of interaction, i.e. an exit of a polyurethane sooligomer (PUR) received at various ratios of initial components.

Table 2

Effects of the ratio of POPG: MDI to the yield of polyurethane sooligomer  
 Таблица 2. Влияния соотношения ПОПГ:ДМДИЦ на выход полиуретанового соолигомера

Name	The reaction mixture				
	1	2	3	4	5
POPG: MDI, mass of the part	100:10	100:15	100:20	100:30	100:40
Output of PUR,% of mass	90.5	92.5	95.6	95.0	94.8

As can be seen from the data in table2 the output of the PUR is significantly influenced by the ratio of POPG: MDI. The optimal ratio of POPG to MDI, which provides the highest yield of PUR (95.6% of may), is 100:20.

An increase in the MDI content in the reaction mixture to 30-40 parts by weight. does not lead to an increase in the output of the PUR. After the exhaustion of the OH groups, MDI remains as an independent component in the system and, as a result of self-structuring, leads to a decrease in the elasticity of the PUR.

PUR, along with high indicators of physical and mechanical characteristics, has high chemical resistance. The thermal stability of PUR at elevated temperatures was studied using differential thermogravimetry (DTG) and differential thermal analysis (DTA) on a derivatograph of the Paulik-Erdei system with a temperature rise from 20 to 500 ° C, at a rate of 5°C per min.

As an inert substance,  $A_{12}O_3$  was used, the weight of the sample was 200 mg (Figure 1). Judging by the DTG curve, from the 120 °C mark from the sample, unreached POPG and MDI are likely to diffuse, with a mass loss of 5%. At a mark of 340°C, the destruction of the sample is fixed, and the mass loss as a whole was 84%.

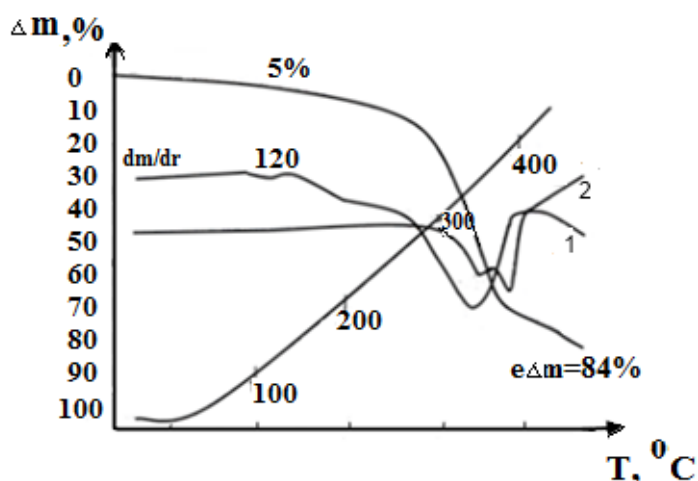


Fig.1. DTA curves of polyurethane. DTA curves of a polyurethane sooligomer (1) and butyl rubber (2).

Рис.1 Кривые ДТА полиуретанового соолигомера(1) и бутилкаучука (2) .

Judging by the DTG curve, from the 120 °C mark from the sample, unrelated POPG and MDI are likely to diffuse, with a mass loss of 5%. At a mark of 340 °C,

the destruction of the sample is fixed, and the mass loss as a whole was 84%. In order to obtain a highly adhesive and highly elastic composite, blends of a polyurethane sooligomer with butyl rubber (BK) have been studied, which have high heat resistance, elasticity, chemical resistance in corrosive environments, and weather and water resistance. It is shown that when mixing PUR with BK, a polymer system is formed, the macromolecules of which mechanically interact to form the so-called interpenetrating meshes.

The ground, suspended BC was placed in a laboratory reactor (V=2.0L) with toluene (or xylene) and stirred at 40-50 °C for 2-3 h until complete dissolution. After the BC was completely dissolved into the solution, 4,4'-diphenylmethane diisocyanate was added at a certain ratio of the components and stirred for 1.5-2 hours, after which the mixture was added to the mixture and stirred for another 50-60 minutes at room temperature. Compositions of compositions with different component ratios are given in table 3.

Table 3

Compositions of compositions based on mixtures of a solution  
Таблица 3. Составы композиций на основе смесей раствора

Name	Composition of mixtures		
	1	2	3
Components, parts by weight: 5% solution of BC in:			
toluene	100	100	100
POPG	100	100	100
<b>MDI</b>	10	15	20

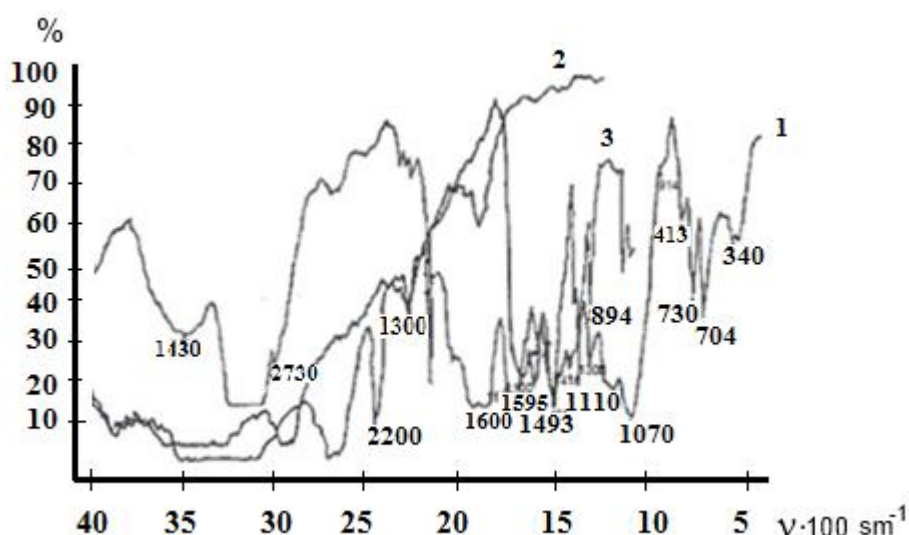


Fig.2. IR spectators of polyurethane sooligomer (1), butyl rubber (2), and mixtures of PUR with BK (3)

Рис.2. ИК секторы полиуретанового соолигомера (1), бутил каучука (2), и смеси ПУСО с БК (3)

Of greatest interest was compositional mixture 3. The IR spectrum spectrophotometer Specord-75 JR) of the sooligomer of POPG and MDI (Fig. 2) was obtained by pressing it together with KBr. The components were taken in a ratio of 300 mg salt and 2 mg test sample of the sooligomer. The tablets were pressed at a pressure of 0.8 MPa. In the region of  $1660\text{ cm}^{-1}$ , the absorption of C=O, and C=N-bonds is manifested. The C=N-band frequency ( $1700\text{ cm}^{-1}$ ) is shifted to the liquid-frequency region due to the conjugation of the C-NH group. In the spectrum of the mixture of the sooligomer and butyl rubber (Fig.2.,cf.3), absorption in the  $2900\text{ cm}^{-1}$   $1400\text{-}1300\text{ cm}^{-1}$ . A band of  $1710\text{ cm}^{-1}$  appeared corresponding to the C=O-group not associated with the NH group. The absorption of  $930\text{ cm}^{-1}$ , associated with  $\text{NH}_2$ -deformation vibrations, increased. In all likelihood, in the formation of the composition, the CN bond is broken and the butyl rubber units are attached at the bond breakage sites.

The thermal characteristics of the compositions are presented on the derivatogram (Fig.3.). Two endoeffects were recorded on the DTG curve: one at  $150\text{ }^\circ\text{C}$ , accompanied by a 7.1 mass loss. Evidently, the solvent diffuses out of the composition. The second peak of the DTG curve corresponds to a temperature of  $635\text{K}$ , which probably indicates the beginning of the destruction of the composition, the mass loss is about 80%.

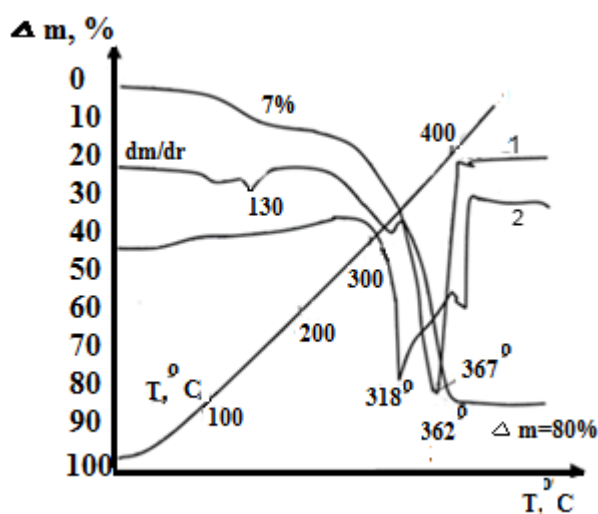


Fig.3. Differential-thermal analysis curves for thermo-oxidative degradation of a polyurethane sooligomer composition (1) and a mixture of a polyurethane sooligomer with butyl rubber (2).

Рис.3. Кривые дифференциально-термического анализа при термо-окислительной деструкции композиции полиуретанового соолигомера(1) и смеси полиуретанового соолигомера с бутилкаучуком(2).

Comparison of the differential thermal analysis data of the sooligomer and the sooligomer + BC composition shows that the resulting composition is thermally more stable than the sooligomer. The physic-mechanical properties of the obtained compositions have been studied, the results of which are presented in table 4.

Table 4

Physic-mechanical properties of compositions of sooligomer + BC  
 Таблица 4. Физико-механические свойства композиций полиуретанового  
 соолигомера с бутилкаучуком

Indicators	Composition		
	1	2	3
Tensile strength, MPa	24.0	25.0	26.0
Conditional voltage, MPa:			
at 100% elongation	11.0	11.7	12.5
at 300% elongation	17.0	18.1	22.5
Relative elongation,%	500	340	350
Residual elongation,%	40	45	20
Tear resistance, N / mm	41	54	60
Adhesive strength, kN / m	6.0	7.4	8.0
Shorehardness, usl. units	83	87	90
Chemical resistance:			
In H <sub>2</sub> SO <sub>4</sub> (5%)	+	+	+
In HNO <sub>3</sub> (10%)	+	+	+
In HCl (30%)	-	-	+

Taking into account the values of IR, DTA, TGA and the results of table, it is seen that (composition 3) based on a mixture of BK+POPG+MDI (100+100+20 parts by weight), a highly adhesive polymer composition has been obtained which has improved physical and mechanical properties.

### RESULTS AND DISCUSSION.

Combining the sooligomer with butyl rubber (copolymer of isobutylene and isoprene) increases the elasticity of the system, removes shrinkage and improves thermal and chemical resistance. A mixture of a sooligomer with butyl rubber is recommended as a highly adhesive and highly elastic coating, an adhesive and a sealing composition.

This composition is also the most stable in aggressive environments, which makes its application promising. The compositions obtained by this way can be used in the manufacture of polymer products for the oil and machine building industries.

The kinetics of sopolycondensation was studied, polyoxydepropylenglycol-sooligomers and 4,4'-diphenylmethanedusothionats were obtained. It was found that the reaction of urethane formation proceeds according to migration polymerization, based on the addition of mobile hydrogen atoms of the polyester to the nitrogen atom. The morphology of synthesized sooligomers was studied by IR spectroscopy. It is shown that combining the sooligomer with butyl rubber (copolymer of isobutylene and isoprene) increases the elasticity of the system, removes shrinkage and improves thermal and chemical resistance. A mixture of a sooligomer with butyl rubber is recommended as a highly adhesive and highly elastic coating, an adhesive and a sealing composition.



## REFERENCES

1. **Maslyuk A.F, Sonina N.I.** Synthesis and properties of static polymerizable multifunctional oligourethanes and polymers based on them. // Plastic masses. 1990. N 8. P. 17
2. **Bilalov Y.M., Shykhaliyev K.S.** Preparation of adhesive compositions based on polymers. Uch.posobie. 2010. 185p.
3. **Askadsky A.A.** The influence of strong intermolecular and chemical interactions on the compatibility of polymers. // Advances in chemistry. 1999. N 4. P. 349-364.
4. **Bilalov Y.M., Abbasov A.M, Safarov M.A.** Preparation of heat-resistant compositions based on modified mixtures of elastomers. In book: Modification of polymers and composite materials based on them for the oil and petrochemical industries. Baku: 2002. P. 84-93
5. **Kurbanova N.I, Seidov N.M.** New composite materials based on modified binary mixtures of elastomers //Azerb. chem. Journal. 2008. N 2. P. 112-116.
6. **Kurbanova N.I.** Composite Materials Based on Modified Unsaturated Elastomers // Azerb. chem. Journal. 2006. N 3. P. 52-57.
7. **Semchikov Y.D.** High-molecular compounds, M.: Izd. "Academy" 2008, 368p.
8. **Mustafaeva R.E** Preparation of heat-resistant rubbers based on mixtures of elastomers. / Abstracts of the scientific conference devoted to the 100th anniversary of Academician M.F. Nagiyev. Baku: 2008. P. 224-225
9. **Musaeva E.E, Bilalov Y.M., Alieva S.F** Atmosphere-protective coatings for elastic surfaces based on elastomer mixtures // Industrial production and use of elastomers. 2009. N 1 P. 15-20
10. **Movlaev I.G, Ibragimova S.M, Babaeva R.E.** Ozone resistant rubber based on a mixture of elastomers. / The eighth scientific-practical conference "Rubber industry. Raw materials, materials, technologies." Abstracts of papers May 14-18. 2001. Moscow. P. 256-257
11. **Makarova D.N, Makarov T.V,** Effect of technological additives on the viscosity of compositions based on butyl rubber. // Rubber and rubber. 2008. N 2. P. 20-22.
12. **Kurenkov V.F.** Chemistry of macromolecular compounds. Publishing Editorial Board "Butlerov Communications" Kazan. 2004. 146 p.
13. **Kurbanova N.I, Seidov N.M.** New composite materials based on modified binary mixtures of elastomers // Azerb. chem. Journal. 2008. N 2. P. 112-116.
14. **Kurbanova N.I.** Modification of unsaturated elastomers by functionally substituted carboxylic acids. // Processes of petro chemistry and oil refining. 2004. N 4. p. 64-68.
15. **Kuleznev V.N, Shershnev V.A.** Chemistry and physics of polymers. Recycling and additional. 2nd ed., Moscow: 2007. 367 p.
16. **Kuleznev V.N.** Mixtures and alloys of polymers. Moscow: Chemistry. 2013. 304 p.
17. **Kudryavtsev Y.V., Plate N.A., Litmanovich A.D.,** Macromolecular reactions in melts and polymer mixtures. Theory and Experiment Moscow: Nauka. 2008. 380 p.
18. **Kryzhanovskiy V.K., Kerber M.L, Burlov V.V.** Manufacture of plastic products. Publishing profession. St. Petersburg. 2011. 460 p.
19. **Kahramanly Y.N., Bilalov Y.M.** Investigation of the properties of incompatible polymer mixtures modified with a compatibilizer // Plastic masses. 2011. N 6. P. 53-58
20. **Ibragimova M.D.** Polyfunctional monomers, macro-monomers and products of their transformations // Processes of petro chemistry and oil refining. 2008. N 4. P. 98-111.
21. **Ermakov S.N., Kravchenko T.P,** Molecular polymer-polymer compositions. Some aspects of getting. // Plastic masses. 2003. N 12. P. 21-26

22. **Bilalov Y.M., Agakishieva M.A., Alieva S.F.** Chemistry and physics of high-molecular compounds. Uch. allowance, Baku: 2012. 141p.
23. **Kiyanenko EA, Zenitova LA** Physical and mechanical properties of polyurethane coatings filled with solid inorganic wastes // Bulletin of Kazan Technological University. 2011. P. 92-96
24. **Kovalevskaya, I.V.** Modification of polyurethane sealants with dispersed inorganic fillers // Bulletin of Kazan Technological University. 2010. N 1. P. 13-19

#### ЛИТЕРАТУРА

1. **Маслюк А.Ф., Сони́на Н.И.** и др. Синтез и свойства статических полимеризационно способных многофункциональных олигоуретанов и полимеры на их основе. // Пластические массы. 1990. № 8. С. 17
2. **Билалов Я.М., Шыхалиев К.С.** Получение клеевых композиций на основе полимеров. Уч.посobie. 2010. 185 с.
3. **Аскадский А.А.** Влияние сильных межмолекулярных и химических взаимодействий на совместимость полимеров. // Успехи химии. 1999. № 4. С. 349-364.
4. **Билалов Я.М., Аббасов А.М., Сафаров М.А.** Получение термостойких композиций на основе модифицированных смесей эластомеров. В кн.: Модификация полимеров и композиционных материалов на их основе для нефтяной и нефтехимической отраслей. Баку: 2002. С. 84-93
5. **Курбанова Н.И., Сеидов Н.М.** Новые композиционные материалы на основе модифицированных бинарных смесей эластомеров //Азерб. хим. журн. 2008. № 2. С. 112-116.
6. **Курбанова Н.И.** Композиционные материалы на основе модифицированных ненасыщенных эластомеров // Азерб. хим. журн., 2006. № 3. С. 52-57.
7. **Семчиков Ю.Д.** Высокомолекулярные соединения, М.: Изд. «Академия» 2008. 368с
8. **Мустафаева Р.Э.** Получение термостойких резин на основе смесей эластомеров. / Тезисы докладов научной конференции, посвященной 100-летию юбилею Академика М.Ф. Нагиева. Баку: 2008. С. 224-225
9. **Мусаева Э. Э., Билалов Я. М., Алиева С. Ф.** Атмосферно-защитные покрытия для эластичных поверхностей на основе смесей эластомеров // Промышленное производство и использование эластомеров. 2009. № 1. С. 15-20
10. **Мовлаев И.Г., Ибрагимова С.М., Бабаева Р.Э.** Озоностойкие резины на основе смеси эластомеров. / Восьмая научно-практическая конференция «Резиновая промышленность. Сырьё, материалы, технологии». Тезисы докладов 14-18 мая 2001. Москва. С. 256-257
11. **Макарова Д.Н., Макаров Т.В.,** Влияние технологических добавок на вязкость композиций на основе бутилкаучука. // Каучук и резина. 2008. № 2. С. 20-22.
12. **Куренков В.Ф.** Химия высокомолекулярных соединений. Издательство Редакция “Бутлеровские сообщения” Казань 2004. 146 с.
13. **Курбанова Н.И., Сеидов Н.М.** Новые композиционные материалы на основе модифицированных бинарных смесей эластомеров //Азерб. хим. журн., 2008. № 2. С. 112-116.
14. **Курбанова Н.И.** Модификация ненасыщенных эластомеров функционально-замещенными карбоновыми кислотами // Процессы нефтехимии и нефтепереработки. 2004. № 4. С. 64-68.
15. **Кулезнев В.Н., Шершнев В.А.** Химия и физика полимеров. Перераб. и доп. 2-е изд., М.: 2007. 367 с.

16. **Кулезнев В.Н.** Смеси и сплавы полимеров. М.: Химия. 2013. 304 с.
17. **Кудрявцев Я.В., Платэ Н.А., Литманович А.Д.,** Макромолекулярные реакции в расплавах и смесях полимеров. Теория и эксперимент М.: Наука. 2008. 380 с.
18. **Крыжановский В.К., Кербер М.Л., Бурлов В.В.** Производство изделий из полимерных материалов. Издательство профессия. Санкт-Петербург. 2011. 460 с.
19. **Кахраманлы Ю.Н., Билалов Я. М.** Исследование свойств несовместимых полимерных смесей, модифицированных компатибилизатором // Пластические массы. 2011. № 6. С. 53-58
20. **Ибрагимова М.Д.** Полифункциональные мономеры, макро-мономеры и продукты их превращений // Процессы нефтехимии и нефтепереработки. 2008. № 4. С. 98-111.
21. **Ермаков С.Н., Кравченко Т.П.** Молекулярные полимер-полимерные композиции. Некоторые аспекты получения. // Пластические массы. 2003. № 12. С. 21-26.
22. **Билалов Я.М., Агакишиева М.А, Алиева С.Ф.** Химия и физика высокомолекулярных соединений. Уч. пособие, Баку: 2012. 141с.
23. **Кияненко Е.А., Зенитова Л.А.** Физико-механические свойства полиуретановых покрытий, наполненных твердыми неорганическими отходами// Вестник Казанского Технологического Университета. 2011. С. 92-96
24. **Ковалевская, И.В.** Модификация полиуретановых герметикой дисперсными неорганическими наполнителями// Вестник Казанского Технологического Университета. 2010. № 1. С. 13-19

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