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ВЛИЯНИЕ НАПОЛНИТЕЛЕЙ НА СВОЙСТВА ОДНОУПАКОВОЧНЫХ ПОЛИУРЕТАНОВЫХ ГЕРМЕТИКОВ В ПРИСУТСТВИИ ЛАТЕНТНОГО ОТВЕРДИТЕЛЯ

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В работе исследовано влияние наполнителей на технологические свойства полиуретановых герметиков и физико-механические свойства отвержденных влагой воздуха герметиков. Представлена технология производства герметика, обоснована последовательность загрузки компонентов в диссольвер. Отмечено, что введение катализатора и латентного отвердителя в систему необходимо осуществлять после введения наполнителя, на последнем этапе смешения при температуре не выше 30 ºС, чтобы предотвратить преждевременное сшивание герметика в процессе его производства. Представлена схема отверждения полиуретанов, в том числе в присутствии латентного отвердителя. Установлено, что при наполнении в пределах 20-80 масс.ч. на 100 масс.ч. предполимера общий комплекс физико-механических показателей остается высоким. При введении минерального дисперсного наполнителя увеличивается напряжение при раздире, но падает относительное удлинение при разрыве. Увеличение прочности при растяжении происходит до определенного предела, после которого наблюдается снижение прочности герметика. Показано, что исходя из значения маслоемкости наполнителей можно оценить вид и количество наполнителя для герметика, т.к. маслоемкость напрямую зависит от размера частиц наполнителя, площади поверхности и формы частиц. Отмечено, что для сохранения высоких физико-механических свойств композиции и оптимальной вязкости герметика лучше сочетать два вида наполнителя разной маслоемкости. Установлено, что применение наполнителей с высокой и низкой маслоемкостью положительно влияет на технологические и эксплуатационные свойства герметиков. Наполнитель с высокой маслоемкостью придает герметику тиксотропность, а наполнитель с низкой маслоемкостью позволяет создать более высоконаполненную композицию с сохранением высоких прочностных показателей.

Ключевые слова: одноупаковочный герметик, полиуретан, отверждаемые герметики, реакционноспособные предполимеры, наполнители, латентный отвердитель, маслоемкость

EFFECTS OF FILLERS ON PROPERTIES OF ONE-PART POLYURETHANE SEALANTS WITH PRESENCE OF A LATENT CURING AGENT

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In this study, the effects of fillers on the technological properties of polyurethane sealants and the physical and mechanical properties of air moisture curing sealants are investigated. The sequence of loading the components in the dissolver, factoring in the presence of a latent curing agent, is demonstrated. It was found that when filling within 20-80 parts weight per 100 parts weight of the pre-polymer, the general complex of physical and mechanical properties remains

high. With the introduction of mineral dispersed filler, the tear strength increases, but the relative elongation at break decreases. The increase in the tensile strength occurs up to a certain limit, after which there is a decrease in the strength of the sealant. It was shown that based on the oil absorption value of the fillers, the type and the amount of a filler for the sealant can be evaluated, as oil absorption directly depends on the particle size, surface area and particle shape of the filler. It was observed that for maintaining high physical and mechanical properties of the composite and the optimum viscosity of the sealant, it is preferable to combine two kinds of fillers with different oil absorption. It was established that the application of fillers with high and low oil absorption has a positive effect on the technological and performance properties of sealants. The filler with high oil absorption contributes to the thixotropy of the sealant, while the filler with low oil absorption allows to form a more highly filled composite while preserving the high strength characteristics.

Key words: one-part sealants, polyurethane, curing sealants, reactive pre-polymers, fillers, latent curing agent, oil absorption

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INTRODUCTION

One of the perspective direction of application of polymeric materials in the construction industry for the effective protection of buildings and structures from environmental influences is the application of sealant materials [1-6].

Sealant is a multicomponent complex composite in which each component performs its essential function; therefore, it is imperative to be guided by scientific evidence-based principles in the selection of the components when formulating a sealant [7-9].

Fillers are second in importance components of a sealant after the coupling agent. A filler is applied primarily to reduce the cost and (or) to add special properties to the sealant, for example, thixotropy, low-density, or fire resistance, etc.; however, the introduction of fillers causes changes in the technological as well as in the performance properties [3, 10, 11].

The objective of this study was is to investigate the effects of conventional fillers on the technological and performance properties of moisture curing polyurethane sealants in the presence of a latent curing agent.

EXPERIMENTAL TECHNIQUES

The polyurethane pre-polymers developed by the author, based on diphenylmethane 4,4'-diisocyanate (MDI) and polyethers with a molecular weight of 2000 and 4500-5000, in the presence of benzoyl chloride used as an inhibitor of intramolecular reactions, were used in the experiment. The content of the NCO-groups in the coupling agent was 4-4.5% [12].

The following were used as fillers: fine calcium carbonate (chalk) MTD-2 (MTD), precipitated calcium carbonate Calofort SV coated with a low percentage (5 percent) of a calcium stearate (CSV), talc MT-GSM (MT), fractionated microdolomite Midol 10-98 (MD), fractionated micromarble Micarb 05-98 (MC05) and Micarb 40 (MC40), aluminum hydroxide Portaflame SG 25 (PSG). The properties of the fillers are displayed in Table [13].

Table

The properties of the fillers

***Таблица.* Свойства наполнителей**

Filler	Particle shape	OA, g/100g	ρ, g/cm^3	D_{50}, mkm
CSV	spherical	300	2.7	0.07
MT	flakey	70	2.0	8
PSG	spherical	22	2.4	25
MD	spherical	16	2.9	10
MC05	spherical	20	2.72	5
MC40	spherical	15	2.72	15
MTD	spherical	16	2.65	7

Diisononylphtalat (DINP) was used as a plasticizer.

A specific problem of one-part sealants is the sensitivity of the pre-polymer to the presence of moisture, and consequently, the need to remove moisture contained in the original materials from the composite [7]. Therefore, the filler was subjected to drying first, and the zeolite based molecular sieve – was introduced to the composite itself.

The loading of the sealant components was carried out as follows: the coupling agent, the plasticizer, the thixotropic agent and the exsiccant were loaded in a mixing tank and mixed. 2-3 portions of the fillers were added while mixing with gradually increasing the speed of rotating milling cutters until a funnel was formed. During spinning, a high pressure zone is formed in front of the teeth of the cutter, and behind them there forms a decompression zone, which leads to the destruction of the agglomerates of particulates (due to friction between the particles themselves) and the increase in temperature; therefore, the mixture was dispersed while cooling (at a temperature of less than 40 °C) in static vacuum (less than 0.2 atm) for 10 min. A little heating is recommended to reduce viscosity, as well as for better dispersion and creating the outlet for air.

Next, a latent curing agent and a catalyst were added to the mixture while mixing and cooling (at a temperature of no higher than 30 °C) and mixed for 2-3 min. This loading sequence allows to avoid premature cross-linking while introducing the catalyst and the latent curing agent to the system.

The tensile strength and the elongation at break tests were conducted on the dumb-bell specimen cut from cured films, in accordance to GOST (All Union State Standard) 270. The sealant was applied to the fluorocarbon plate and evened out using a palette knife with a 2.0±0.2 mm gap [14]. The prepared films were kept for 3 h at a temperature of (23 ± 2) °C, then in a dryer at a temperature of (70±5) °C for (48,0±0,5) h. Before the test, the samples were kept at a temperature of (23 ± 2) °C for no less than 3 h.

RESULTS AND DISCUSSION

As it is known [4, 15, 16], during the filling of polyurethane coupling agents, foaming of the pre-polymer occurs as a result of a curing reaction accompanied by emitting carbon dioxide. To eliminate foaming in moisture curing single component polyurethane systems, latent curing agent can be used [17-19].

The scheme of the curing of polyurethanes in the presence of a latent curing agent is presented in Fig. 1.

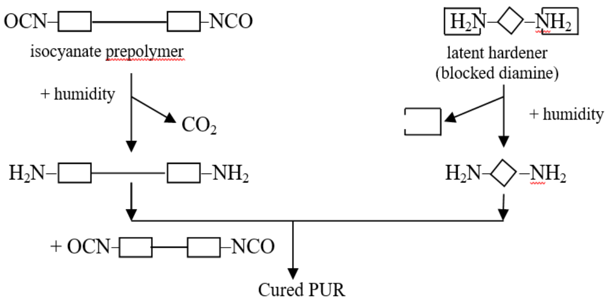

Fig. 1. The scheme of curing of polyurethanes [15]

Рис. 1. Схема отверждения полиуретанов [15]

To suppress bubble formation during curing of isocyanate-containing compositions with latent amine hardeners are: on contact with atmospheric moisture blocked amino latent hardener hydrolyzed and then reacted with the isocyanate groups of the composition without the emission of carbon dioxide.

The effects of fillers on the physical and mechanical properties of the moisture-cured films are presented in Fig. 2-4.

The increase in the physical and mechanical properties of the composite takes place until the amount of a filler added reaches a certain limit. It was observed that this dependency is extreme for all the tested composites. Technological and performance properties will be different in case of filling the sealant up to the same level but with different types of fillers.

It should be noted that for the composites with any of the fillers presented in this study, their tensile strength is higher than that of the composites without fillers. When filling (c_f) in the range from 20 to 80 wt % for 100 pts. wt., the tensile strength (σ) of the pre-polymer increases by approximately 35-40% on average.

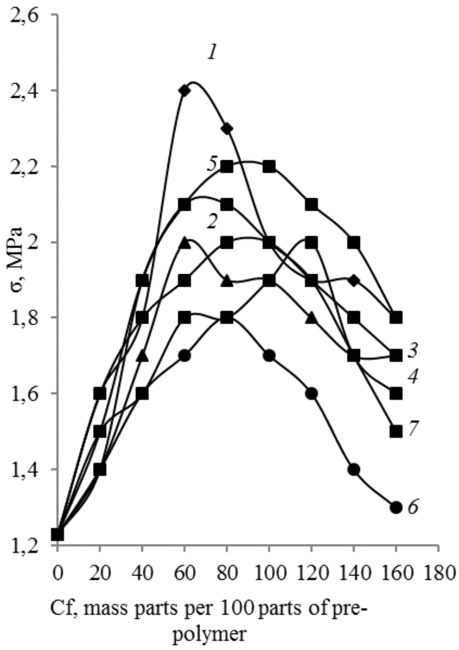

Fig. 2. The effect of fillers content in the sealant on the tensile stress at break of cured films: 1 - CSV; 2 - MT; 3 - PSG; 4 - MD; 5 - MC05; 6 - MC40; 7- MTD

Рис. 2. Влияние содержания наполнителей в герметике на разрушающее напряжение при растяжении отвержденных пленок: 1 - CSV; 2 - МТ; 3 - PSG; 4 - МД; 5 - МК05; 6 - МК40; 7- МТД

The strength-filler amount diagram for the composition containing Calofort SV as a filler has a strongly pronounced extremum in the 60-70 pts. wt region. It should also be noted that precipitated chalk has a more developed surface than other fillers. The oil absorption of Calofort SV is slightly higher than that of other fillers. The highly developed surface of Calofort

SV with a pH of 10-11 leads to a sharper change in the properties of the polymer composite with significantly lower concentrations. In this case, Calofort SV, apparently, plays the role of an active filler.

Similar extremum is observed with aluminum hydroxide, but to a much lesser extent. The rest of the diagrams show a more uniform increase in strength first and then its decrease.

With the increase of the filler amount in the composite, the relative elongation (ε) of the samples slightly increases until filled to 80 pts. wt per 100 pt. wt of the pre-polymer, then it decreases, which is due to the declining ability of macromolecules to the orientation processes at elongating because of the increased density of cross-linking.

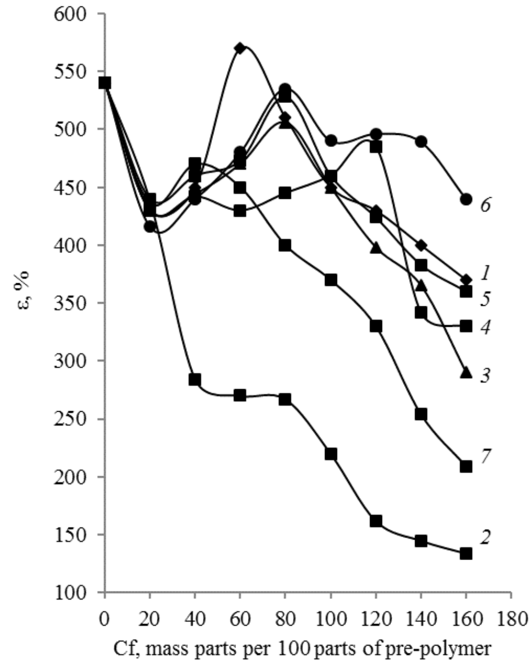

Fig. 3. The effect of fillers content in the sealant on the elongation at break of cured films: 1 - CSV; 2 - MT; 3 - PSG; 4 - MD; 5 - MC05; 6 - MC40; 7- MTD

Рис. 3. Влияние содержания наполнителей в герметике на относительное удлинение при разрыве: 1 - CSV; 2 - MT; 3 - PSG; 4 - МД; 5 - МК05; 6 - МК40; 7- МТД

The elongation – Calofort SV amount diagram has a strong extremum in the 60 pts. wt region. At the same time, the elongation-talc content diagram behaves in a totally different way. When filling with talc, the decrease in elongation may be associated with platelet shape of the particles that interferes with the ability of macromolecules to the orientation processes.

As is known [4], with the introduction of a filler into the composite, the tear strength (σ_s) increases, which is confirmed by the critical tear stress-filler content diagrams. It should be noted that for the composites with Calofort SV and Talc MT-GSM, the diagrams have an extremum, after which the critical tear stress decreases.

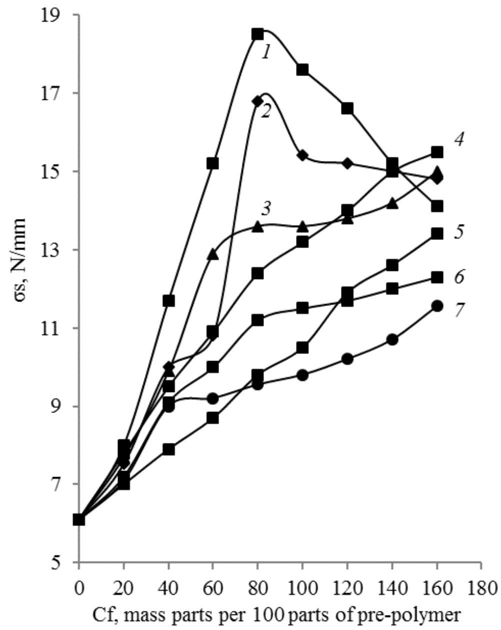

Fig. 4. The effect of fillers content in the sealant on the critical tear stress of cured films: 1 - MT; 2-CSV 3 - PSG; 4 - MTD; 5 - MC05; 6 - MD; 7- MC40

Рис. 4. Влияние содержания наполнителей в герметике на разрушающее напряжение при раздире: 1 - МТ; 2-CSV 3 - PSG; 4 - МТД; 5 - МК05; 6 - МД; 7- МК40

It should be noted [4] that the talc and chemically precipitated chalk - based composites come out “dry” and are of high viscosity, i.e. the system lacks the coupling agent, which is noticeable when filling above 120 pts. wt for 100 pts. wt of the coupling agent.

Thus, the optimal ratio of filler and film-former is of great importance [20]. The amount of film-forming substance, spent on formation of solvation shells and filling the free spaces between the particles surrounded by these shells, is called oil absorption (and is expressed in grams of flaxseed oil per 100 g of filler when mashing to the state of a dense ball.

The lower the oil absorption (OA) of the filler is, the less amount of coupling agent is needed for the preparation of a composite, and the coupling agent can be filled more. It should be noted that the relationship between the coupling agent and the filler affects not only the physical and mechanical properties, but also the viscosity of the sealant.

Fig. 5 shows that with the introduction of fillers with higher oil absorption, there is an increase in viscosity. High oil absorption is typical for fillers with

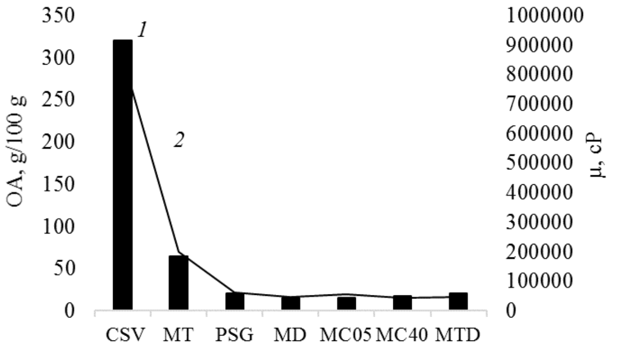

Fig. 5. The effect of the filler oil absorption on the viscosity of the sealant with a content of 160 wt. including filler per 100 wt.h. binder: 1-dynamic viscosity; 2 - oil obsorption of fillers

Рис. 5. Влияние маслоемкости наполнителя на вязкость герметика с содержанием 160 масс. ч. наполнителя на 100 масс.ч. связующего: 1- динамическая вязкость; 2 – маслоемкость наполнителя

small size particles, as well as with the platelet shaped particles. Oil absorption can only describe the compounding formulation of composites very tentatively, because it does not reflect the influence of dispersiveness and particle size of fillers to the full extent, but it allows to approximately estimate the amount of filler, depending operational and technological properties needs to get a sealant.

The filler with high oil absorption gives the sealant thixotropic properties, but extremely reduces the strength characteristics of the sealant. Its thixotropic properties disappear.

CONCLUSIONS

The technology of manufacturing filled sealants in the presence of a latent curing agent was developed.

It was demonstrated, that the introduction of a latent curing agent to the system must be carried out after the introduction of a filler, on the last stage of mixing to prevent premature cross-linking of the sealant.

During the filling of PU pre-polymer in the presence of a latent curing agent, the increase in the sealant strength characteristics up to a certain limit was noted, then there is a decrease in the strength properties. With the introduction of a mineral dispersed filler, the tear strength increases, but the elongation at break decreases.

Based on the physical and mechanical properties of the sealant with different fillers represented in Table 1 and Fig. 2-4, it can be concluded that the amount, size and shape of the filler particles affect the technological and operational properties of the sealant. Oil absorption allows approximately determine the amount of filler depending on the requirements of the sealant.

It was established that the maximum strength performance with thixotropic properties can be achieved in production of sealants based on high and low oil absorption fillers such as precipitated chalk, and microcalcite.

Л И Т Е Р А Т У Р А

1. Европейский рынок клеев и герметиков. *Лакокрас. матер. и их примен*. 2015. № 6. С. 23-25.
2. **Petrie E.M.** Handbook of adhesives and sealants. New Yor. McGraw-Hill. Professional. 2000. 896 p.
3. **Cognard Ph.** Handbook of Adhesives and Sealants. V.1: Basic Concepts and High Tech Bonding. France. Elsevier Ltd. 2005. 511 p.
4. **Майер-Вестус У.** Полиуретаны. Покрытия, клеи и герметики. М.: ООО «Пэйнт-Медиа». 2009. 400 с.
5. **Имамутдинов И.В., Галимзянова Р.Ю., Хакимуллин Ю.Н.** Герметики на основе эластомеров. *Вестн. технол. ун-та*. Казань. 2015. Т. 18. № 6. С. 69-74.
6. **Romanov S.V., Panov Y.T., Timakova K.A.** Polyureas-a new promising class of binders for adhesives, sealants, and coatings. *Polym. Sci. – Ser. D.* 2013. V. 6. N 3. P. 175-180. DOI: 10.1134/S1995421213030209.
7. **Тимакова К.А., Панов Ю.Т., Самойленко В.В.** Принципы составления рецептур полиуретановых герметиков. *Клеи. Герметики. Технологии.* 2015. № 10. С. 2-8.
8. **Müller B., Poth U.** Coatings Formulation. U. Poth. 2nd rev. ed. Vincentz Network. 2011. 287 p.
9. **Брок Т., Гротэклаус М., Мишке П.** Европейское руководство по лакокрасочным материалам и покрытиям. М.: Пэйнт-Медиа. 2007. 548 с.
10. **Szycher M.** Szycher's handbook of polyurethanes. Boca Raton: Taylor & Francis Group CRC Press. 2013. 1092 p.

R E F E R E N C E S

1. European market of adhesives and sealants. *Lakokras. Mater. Ikh Primen.* 2015. N 6. P. 23-25 (in Russian).
2. **Petrie E.M.** Handbook of adhesives and sealants. New Yor. McGraw-Hill. Professional. 2000. 896 p.
3. **Cognard Ph.** Handbook of Adhesives and Sealants. V.1: Basic Concepts and High Tech Bonding. France. Elsevier Ltd. 2005. 511 p.
4. **Meier-Westhues U.** Polyurethanes coatings, adhesives and sealants. M.: Paint-Media LLC. 2009. 400 p. (in Russian).
5. **Imamutdinov I.V., Galimzyanova R.Yu., Khakimullin Yu.N.** Sealants based on elastomers. *Vestn. Tekhnol. Un-ta*. Kazan. 2015. V. 18. N 6. P. 69-74 (in Russian).
6. **Romanov S.V., Panov Y.T., Timakova K.A.** Polyureas-a new promising class of binders for adhesives, sealants, and coatings. *Polym. Sci. – Ser. D.* 2013. V. 6. N 3. P. 175-180. DOI: 10.1134/S1995421213030209.
7. **Timakova K.A., Panov Yu.T., Samoylenko V. V.** Principles of Formulating Techniques for Polyurethane Sealants. *Klei. Germetiki. Tekhnologii.* 2015. N. 10. P. 2-8 (in Russian).
8. **Müller B., Poth U.** Coatings Formulation. U. Poth. 2nd rev. ed. Vincentz Network. 2011. 287 p.
9. **Brock, T., Groteklaus M., Mishka P.** European Guide to Paint Materials and Coatings. M.: Paint Media. 2007. 548 p. (in Russian).
10. **Szycher M.** Szycher's handbook of polyurethanes. Boca Raton: Taylor & Francis Group CRC Press. 2013. 1092 p.

11. **Wolf A.T.** Durability of Building and Construction Sealants and Adhesives. *J. ASTM Internat. Select. Techn. Papers STP1545. ASTM International.* 2010. XVII. 417 p.
12. **Тимакова К.А.** Синтез и свойства полиуретановых предполимеров для однокомпонентных герметиков. Сб. тр. III Всеросс. науч. конф. Химическая наука: современные достижения и историческая перспектива. Казань. 2015. С. 125-130.
13. **Цвайфель Х., Маер Р.Д., Шиллер М.** Добавки к полимерам: Справочник. СПб.: Профессия. 2010. 1144 с.
14. **Воробьева Л.Г., Кофтюк В.А., Листова О.В.** Формирование покрытий на основе полиуретановых лакокрасочных материалов. *Лакокрас. пром-ть.* 2012. № 7. С. 24–28.
15. **Maier S.** Modern PUR sealants and adhesives: superior products thanks to novel curing technology. The 8th World Adhesive & Sealant Conference (WAC 2012). Paris, France. 18-21 September 2012. С. 186-192.
16. **Логинова С.Е., Аверченко Е.Б., Тимакова К.А., Егоров С.Ф.** Современные полиуретановые герметики производства ООО НПФ «Адгезив». *Клеи. Герметики. Технологии.* 2014. № 6. С. 2-5.
17. **Adrian Thomas B.** Improve polyurethane surface coatings using oxazolidines and aldimines. *J. Surf. Coat. Australia*. 2015. V. 52. N 2. P. 6-49.
18. **Carter Neil G.** Scavenge moisture and cut pinholes in a trice – Oxazolidine latent hardeners in polyurethane systems. *Eur. Coat. J.* 2012. N 06. P. 18-21.
19. **Thomas A.** Improving polyurethane surface coatings. Part 2: Use of oxazolidines and aldimines. *Surf. Coat. Internat*. 2015. N 5 P. 223-230.
20. **Ciullo P. A.** Industrial minerals and their uses: a handbook and formulary. USA. Noyes Publications. 1996. 632 p.

11. **Wolf A.T.** Durability of Building and Construction Sealants and Adhesives. *J. ASTM Internat. Select. Techn. Papers STP1545. ASTM International.* 2010. XVII. 417 p.
12. **Timakova K.A.** Synthesis and properties of polyurethane prepolymers for one-component sealants. Collected Works III All-Russian Scientific Conf. Chemical science: Modern achievements and historical perspective. Kazan 2015. P. 125-130 (in Russian).
13. **Zweifel H., Mayer R.D., Schiller M.** Polymer Additives: A Handbook. SPb.: Profession. 2010. 1144 p. (in Russian).
14. **Vorobieva L.G., Koftyuk V.A., Listova O.V.** The formation of coatings based on polyurethane paints. *Lakokras. Prom-t'.* 2012. N 7. P. 24–28 (in Russian).
15. **Maier S.** Modern PUR sealants and adhesives: superior products thanks to novel curing technology. The 8th World Adhesive & Sealant Conference (WAC 2012). Paris, France. 18-21 September 2012. P. 186-192.
16. **Loginova S.E., Averchenko E.B., Timakova K.A., Egorov S.F.** Modern polyurethane sealants manufactured by LLC "Adhesive". *Klei. Germetiki. Tekhnologii.* 2014. N. 6. P. 2-5 (in Russian).
17. **Adrian Thomas B.** Improve polyurethane surface coatings using oxazolidines and aldimines. *J. Surf. Coat. Australia*. 2015. V. 52. N 2. P. 6-49.
18. **Carter Neil G.** Scavenge moisture and cut pinholes in a trice – Oxazolidine latent hardeners in polyurethane systems. *Eur. Coat. J.* 2012. N 06. P. 18-21.
19. **Adrian Thomas.** Improving polyurethane surface coatings. Part 2: Use of oxazolidines and aldimines. *Surf. Coat. Internat*. 2015. N 5 P. 223-230.
20. **Ciullo P. A.** Industrial minerals and their uses: a handbook and formulary. USA. Noyes Publications. 1996. 632 p.

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