Technical characteristics of rigid sprayed PUR and PIR foams used in construction industry

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Abstract. The article describes the distinctive properties of rigid polyurethane foam and polyisocyanurate (PUR and PIR). A brief review of the research was carried out on their modification with an objective to improve the thermal insulation properties and reducing the combustibility. A comparative analysis of the technical characteristics of rigid PUR and PIR foams of various manufacturers is presented. The problems of the state of the market for the production of polyurethane foam and polyisocyanurate in Russia have been marked. It is established that the further development of the fabrication technology of heat-insulating sprayed rigid PUR and PIR foams requires uniformity of technical characteristics of original components and finished products. Moreover, it requires the creation of unified information base for raw materials and auxiliary materials used in the production of PUR and PIR foam.

1. Introduction
The positive effect of combination of properties, reliability and cost-effectiveness of polyurethanes determines the wide practical application of polyurethane foam insulation, and now there is no alternative to similar materials.

Despite the frequent practice and large amount of researches of PIR and PUR foams within its entire development period, there is still no unification of the technical characteristics of original components and a single information base for the raw material systems and auxiliary materials used in the production of PUR and PIR foam.

2. Materials and Methods
Thermal insulating rigid closed-cell PUR and PIR foams can be obtained at the construction site by mixing two components [1]:

- mixture of polyesters (polyols), expanding agents, catalysts, foam regulator and various additives for properties improving;
- isocyanate product (MDI or TDI).

Foams have a cellular structure, commonly containing air, nitrogen, carbon dioxide of 90-95%. Closed pores exclude the occurrence of moisture, mold and rot, unlike open-cell materials. The greatest advantage of these insulating materials is a low thermal conductivity. It amounts to 18-25 mW / (m · K), which is superior to other commercially available insulating materials [2-3].
The foaming of PUR and PIR occurs with the use of expanding agents: freon, pentane, HFC 245fa, CO2 or water. Additives with spraying PUR and PIR foams can be used: flame retardants, fillers, dyes, chain extenders, free fluorine gas agents, which are commonly used to protect the physical integrity of PUR and for staining. They also contribute to its formation or reduce the combustibility of finished products [4, 7]. Depending on the application area in the structure, the thickness of the thermal insulation layer of polyurethane foam varies for obtain the maximum effect and the PUR foam is applied in several layers [5]. PIR is a modified PUR with dominance in the isocyanate group system and another polyl ratio. The proportion of MDI is higher, and instead of polyols on ethers, a polyether polyl is used in the reaction. The catalysts and additives used to produce PIR are also different from those used in PUR [6]. PIR-foams are obtained in a ratio of 1:2 (polyl and isocyanate), PUR-foams in proportions of 1:1. Polymerization of PIR is carried out at a higher temperature than that of PUR. As a result excess isocyanurate reacts with itself, forming stronger and more stable bonds [7].

Advantages of PUR and PIR foams with a closed-cell structure in front of the foam with an open cell are strength, better heat-shielding properties, greater resistance to air and water vapor leaks [8].

Polyurethane foams effectively absorb uncharged, large, hydrophobic molecules, such as naphthalene, pyrene, benzopyrene. The sorption properties of polyurethane foams change as a result of the modification of their surface by various reagents. Polyurethane foams, modified with organic compounds (organic reagents) forming stable complexes with metals, extract them more efficiently than unmodified [9]. Polyurethane foam modified by ceramic nanoparticles [10] revealed general patterns of density, hardness, strength and elongation at failure, as well as resistance to abrasion of polyurethane foams depending on the filler (its kind and time of mechanochemical treatment).

It has been found that the influence of bio-products such as corn starch, rapeseed glycerin, and oil-based propylene glycol as bifunctional and trifunctional chain extenders has a higher long-term water absorption compared to polyurethane foams. Foams containing 5-25% corn starch show significantly lower values of the density and compressive strength, as well as the cell size compared to the foam polyurethane foam. The greatest compressive strength and low thermal conductivity are obtained for foams with 25% of rapeseed glycerol [11].

Various biocompatible materials, such as rapeseed oil and tall oil, could be the raw material for the production of polyurethane foams according to [12]. Usually reducing the inflammability of PUR materials is achieved by the addition of flame retardants, halogen-containing compounds and phosphates. It can be considered that halogenated flame retardants release volatile compounds from materials and release toxic gas products during combustion. The addition of thermally expandable graphite reduces the toxicity of the reaction products formed. The various expandable graphite flame retardants provided a significant reduction in flammability while maintaining the low thermal conductivity of the insulating materials. Fine dispersible converter slags can be considered as effective fillers in rigid foam polymeric compositions and used to improve the construction and technical properties filled with polyurethane foams in order to use them as a thermal-insulating layer in composite metal tiles [13]. The fabrication of roofing elements was carried out in the Lipetsk region and it is characterized by a significant economic effect. At the present time in Europe, DowChemical company conducts research on polyisocyanurate foams [14], and the American chemical Huntsman company has also investigated the effect of the ingredients of the polysisocyanurate formulation on their effectiveness [15-16]. The issue of economic validity and efficiency of the use of various sprayed polyurethane foam was raised in scientific works [17-22], in the conclusions of which one can observe a positive evaluation of the use of various forms of polyurethane foam in the construction field.

In [23] the analysis of technical and economic efficiency of polyurethane foam was compared with traditional mineral wool. Thus, the coefficient of thermal conductivity of closed-cell PUR foam has limits of 0.018-0.03 W/m with a coating thickness of 5 to 70 mm, the mineral wool has open pores with coefficients 0.05-0.07 W/m (dry) and 0.18 W/m (wet) and a thickness of 120 - 220 mm. Effective lifetime of PUR foam is 25 - 50 years and for mineral wool it is 5 years. Also PUR foam is more resistant to aggressive environments and is environmentally safe. The working temperature of polyurethane foam, depending on its mark, is in the range from -80 to +1500 C, (mineral wool from -40 to +1200 C).
The PU foam has excellent adhesion to brick, concrete, metal, wood, on average 2 kg/cm², which is absence for mineral wool. Also PUR and PIR foams as insulation materials have advantages, such as the absence of "cold bridges" in the case of seamless thermal insulation, the possibility of manufacturing heat-insulating "shells" of a given shape by pressing the liquid PUR [24]. Advantages and modifications of rigid sputtered polyurethane foams and polyisocyanurates were studied in [25-39].

3. Discussion
For rigid PUR and PIR foams with closed cells, the technical characteristics of large chemical producers are analyzed. Selected foreign companies are major manufacturers of rigid PUR and PIR foams and component suppliers for Russian companies.

The main parameters of rigid closed cell PUR and PIR foam correspond to the values indicated in Tables 1 to 4. For clarity, the most important characteristics of PUR and PIR foams of various companies are presented, which have the most significant differences.

Table 1. Comparative analysis of density.

| Product | Density, kg/m³ | Company | Method |
|---------|---------------|---------|--------|
| PUR EX NG | 35 – 65 | Polychem System | |
| Elastospray (Lupranate M20S) | 32-61 | BASF | |
| Baymer Spray 150 | 32 | | EN 1602 |
| Desmodur 44V20L (Desmodur VKS 20 F) | 53 | Covestro - Bayer | |
| Baymer Spray 300 | | | |
| Daltotherm +Suprasec | 30-65 | Huntsman | EN ISO 845 |
| Extrafoam TS 22011 | 35-45 | | |
| Extrafoam TS 22012 | 50-60 | | |
| China | Wanefoam (Wannate PM-200) | 30-50 | Wanhua ChemicalGroup | |
| USA | | | |

As can be seen from the data given, the rigid PUR and PIR foams have a density in the range of 30-70 kg/cm³. This density range is used for thermal insulation and noise insulation. Ultra-dense species from 70 kg/cm³ are used for waterproofing in the foundations of buildings, as well as on other surfaces where the service life of the material is more than 50 years. The higher the density of PUR and PIR foams, the longer the term of their use.

Table 2. Comparative analysis of thermal conductivity.

| Product | Thermal conductivity, W/(m·K) | Company | Method |
|---------|-------------------------------|---------|--------|
| PUR EX NG | 0.023 | Polychem System | |
| Elastospray (Lupranate M20S) | 0.028 | BASF | |
| Baymer Spray 150 | | | EN 12667 |
| Desmodur 44V20L (Desmodur VKS 20 F) | 0.028 | Covestro - Bayer | |
| Baymer Spray 300 | | | |
| USA | Daltotherm+Suprasec | 0.023 | Huntsman | EN 12667 |
| Extrafoam TS 22011 | 0.023 | | |
| Extrafoam TS 22012 | 0.021 | | DIN 52612 |
| China | Wanefoam (Wannate PM-200) | 0.023 | Wanhua ChemicalGroup | - |
The thermal conductivity of PUR and PIR foams is in the range 0.021-0.028 W/(m * K). These manufacturers do not have a uniform thermal conductivity characteristics, and this leads to confusion when choosing a thermal insulation material.

**Table 3.** Comparative analysis of Compressive strength.

| Product                  | Compressive strength, kPa | Company                  | Method   |
|--------------------------|---------------------------|--------------------------|----------|
| PUREX NG                 | 200                       | Polychem System          |          |
| Elastospray (Lapranate M20S) | 150-400                   | BASF                     |          |
| Baymer Spray 150         | 140                       | PolyurethanesEurope      |          |
| Desmodur 44V20L (Desmodur VKS 20 F) | 300               | Covestro - Bayer         |          |
| Baymer Spray 300         |                           |                          | EN 826   |
| Daltotherm+Suprasec      | 240-390                   | Huntsman                 | EN ISO 844|
| Extrafoam TS 22011       | 150                       |                          |          |
| Extrafoam TS 22012       | 300                       |                          |          |

USA

| Product                  | Water absorption, % | Company                  | Method   |
|--------------------------|---------------------|--------------------------|----------|
| PUREX NG                 | 2                   | Polychem System          |          |
| Elastospray (Lapranate M20S) | 2                | BASF                     |          |
| Baymer Spray 150         | 2                   | PolyurethanesEurope      | EN 12087 |
| Desmodur 44V20L (Desmodur VKS 20 F) | 2          | Covestro - Bayer         |          |
| Baymer Spray 300         |                     |                          | USA      |
| Daltotherm+Suprasec      | 1.4                 | Huntsman                 | EN 1609  |
| Extrafoam TS 22011       | 3.5                 |                          | DIN 53428|
| Extrafoam TS 22012       | 3.5                 |                          |          |

China

| Product                  | Water absorption, % | Company                  | Method   |
|--------------------------|---------------------|--------------------------|----------|
| Wanefoam (Wannate PM-200) | 1.3                | Wanhua ChemicalGroup     | -        |

The compressive strength of rigid PUR and PIR foams is 150–400 kPa. Large compression resistance values are relevant for materials of higher density and are used where the service life of the material is more than 50 years. For densities of 30-70 kg/cm3 correspond to 150-400kPa, for denser values there corresponds a value of more than 400 kPa. Uniformity of this characteristic among companies is absent.

**Table 4.** Comparative analysis of water absorption

| Product                  | Water absorption, % | Company                  | Method   |
|--------------------------|---------------------|--------------------------|----------|
| PUREX NG                 | 2                   | Polychem System          |          |
| Elastospray (Lapranate M20S) | 2                | BASF                     |          |
| Baymer Spray 150         | 2                   | PolyurethanesEurope      | EN 12087 |
| Desmodur 44V20L (Desmodur VKS 20 F) | 2          | Covestro - Bayer         |          |
| Baymer Spray 300         |                     |                          | USA      |
| Daltotherm+Suprasec      | 1.4                 | Huntsman                 | EN 1609  |
| Extrafoam TS 22011       | 3.5                 |                          | DIN 53428|
| Extrafoam TS 22012       | 3.5                 |                          |          |

China

| Product                  | Water absorption, % | Company                  | Method   |
|--------------------------|---------------------|--------------------------|----------|
| Wanefoam (Wannate PM-200) | 1.3                | Wanhua ChemicalGroup     | -        |

Analysis of the water absorption characteristics of the material has values in the range of 1.3-3.5%. Uniformity of this characteristic among companies is absent. Russian companies, as a rule, produce PUR and PIR on the basis of imported isocyanate, which is mixed with a Russian-made polyol. The maximum operational temperatures for PUR and PIR are +100°C and +150°C respectively. Polyisocyanurate has reduced fire hazard due to included fire retardant does not provide combustion and damps by itself in the absence of a source of fire. Besides, polyisocyanurate is more sustained to the effect of solar radiation compared to PUR [40]. Wooden tile dimensions of 1000*1000*10 mm with density of 500 kg/m3 during complete combustion provides a heat of combustion of 80 MJ. Heat of combustion of polyurethane foam of the same dimensions with density of 50 kg/m3 is estimated at 13.5 MJ, i.e. the contribution of PUR to the thermal balance of the fire is 6 times less than that of a tree [40].
The sprayed polyurethane foams emit CO, CO2, HCN and nitrogen oxides during combustion. Researches [40] have confirmed the lower toxicity of PUR combustion products compared to products released during the burning of wood, cork, wool, cotton fabrics, plywood, particle board. The lower emission of HCN in the case of PUR combustion is explained by the fact that when the PUR is softened in the combustion zone, a liquid viscous mass containing hydrogen cyanide is formed, so that it can decompose, which leads to a decrease in the toxicity of the combustion products. Also, when the flame is applied to the PUR and PIR foams, the outer layer of the material is charring to form a "porous" carbon matrix that prevents the burning of the inner layers of polymers. Due to the low thermal conductivity and the closed porous structure, the polyurethane foam does not immediately burn down to the full depth. An important factor is also the fact that the density of polyurethane foam is ten times less than that of wood, i.e. in a unit of volume less than the product to be burned. Thus, if we compare PIR, which are products of the new generation, with traditional PUR systems, PIR fillers have reduced flammability. PIR when exposed to a flame instantly becomes coked and prevents the spread of fire. This provides high fire and technical indicators of both materials and structures where it is used. In the case of using heaters in structures, the material occupies an average niche between mineral wool and expanded polystyrene by its parameters [17, 41].

3.1. Production of polyurethanes in Russia
The market of polyurethanes in Russia remains dependent on the supply of imported raw materials. There is a decision of the Ministry of Industry and Trade to include the project of MDI production in the plan for import substitution in the chemical industry. Estimated period of implementation - 2020. At the end of 2016, the import of isocyanates in Russia amounted to 157.2 thousand tons, which is 1.5% more than in the previous year. Of this volume, the main bulk is MDI - 113.6 thousand tons. However, in comparison with the indicator of 2015, the import of MDI fell by 0.7%. The import of TDI grew by 2.2% and reached 39 thousand. In the structure of Russian buyers of imported isocyanates last year, «Dow Isolan» is ranked first, and «Elastokam» takes second place. DowEurope, WanhuaChemical and BASF are among the largest suppliers of MDI. Covestro, BASF and BorsodChem are leaders on import TDI to Russia. An important change in the structure of polyurethane production in Russia over the past 12 years from 2004 to 2016 is the increased overall in output by 47% (from 187 thousand tons to 275 thousand tons) [42]. At the end of 2016, the volume of the market of the sprayed polyurethane foam in Russia is amounted to 8.6 thousand tons. At the moment, the market of the sprayed polyurethane foam is 0.7% of the TIM market and may double in upcoming years. In general, the polyurethane industry in Russia is currently developing, but at the same time it has certain problems. Russian PPU consumption in construction is below the European level, however, the market tends to this high level. To do this, it is first of all necessary to popularize the product and to participate more actively in the improvement of technical regulation in terms of energy efficiency and fire safety [42].

3.2. Normative base of production and application of sprayed PUR and PIR foam
There are no standards for the production and using of polyurethane foam and polyisocyanurate in Russia. Each manufacturer produces products according to its own specifications Standards for the production and usage of polyurethane foam and polyisocyanurate in Europe and the USA: - BS EN 14315-1: 2013 - Thermal insulating products for buildings - locally produced rigid polyurethane foam (PUR) and polyisocyanurate (PIR) - European standard [43]; - ASTM C1289 - 16a – Standard Specification for Faced Rigid Cellular Polyisocyanurate Thermal Insulation Board - American Standard [44]; - ASTM C1029 - 15 – Standard Specification for Spray-Applied Rigid Cellular Polyurethane Thermal Insulation - American Standard [45].

BS EN 14315-1: 2013 refers to series of standards for locally produced insulation materials such as mineral wool, expanded clay, expanded perlite, expanded vermiculite, polyurethane / polyisocyanurate, cellulose, bound expanded polystyrene and expanded polystyrene used in buildings. Also, the standard specifies the requirements for rigid polyurethane foam (PUR) and polyurethane foam (PIR), sprayed
and received on site when applied to walls, ceilings, roofs, suspended ceilings and floors. This normative document, compared to American ASTM C1289-16a and ASTM C1029-15, covers a wide range of applications and has more detailed information about test methods, control procedure and marking. However, the standard does not indicate the values of all product characteristics required for a particular application of the product.

4. Conclusions
At present, heat-insulating rigid PUR and PIR foams produced in the construction site by mixing components are promising thermal insulation materials. An analysis of the technical characteristics of large PUR and PIR manufacturers shows that the lack of uniformity of the technical characteristics of PUR and PIR foam and the lack of a unified approach in brands and types of materials from companies are misleading consumers. At the present time in Russia, most of the raw components for PUR and PIR foam are purchased abroad (due to no import substitution) and the brands have different names for each of the companies.

References
[1] Pustovgar, A., Tanasoglo, A., Garanzha, I., Shilova, L., Adamtsevich, A. 2016 MATEC Web of Conferences, 86, art. no. 04003 (2016). DOI: 10.1051/matecconf/20168604003
[2] Asheychik A 2016 Experimental study of composite materials (SPb: SPbPU) 91p
[3] http://www.polyurethanes.basf.de/pu/solutions/de/function/conversions:/publish/content/group/Arbeitsgebiete_und Produkte/Thermoplastische_Spezialelastomere/Infomaterial/elastollan_material_ru.pdf
[4] Zhukov A, Smirnova T, Chugunkov A and Himich A 2013 The Bulletin of MGSU 5 C 96-102
[5] Berlin A and Shutov F 1978 Penopolymers based on reactive oligomers (St. Petersburg: Nauka) Since 296
[6] Adamtsevich, A., Eremin, A., Pustovgar, A., Pashkevich, S., Nefedov, S. 2014 Applied Mechanics and Materials, 670-671, pp. 376-381 DOI: 10.4028/www.scientific.net/AMM.670-671.376
[7] Kerch Yu 1979 Physical chemistry of polyurethanes (Kiev: Nauk Dumka)
[8] Dmitrienko S Apiary In 2010 Polyurethane foams: sorption concentrating and application in chemical analysis (Moscow) 264 s
[9] Voloskova E, Poluboyarov V, Gorbunov F, Guryanova T, Andryushkova O and Goncharova A 2010 Bulletin of the Kemerovo State University 1 pp. 8-12
[10] Kairytė A, Vaitkus S and Balčiūnas G 2016 Engineering structures and technologies 8 Pp 101-107
[11] Kirpluks M, Cabulis U and Avots A 2016 Latvian State Institute of Wood Chemistry Riga, Latvia pp 85-111
[12] Korneev A, Goncharov M and Statalov G 2014 Building Materials 3 pp 92-95
[13] URL: http://www.dow.com/scripts/litorder.asp?filepath=/polyurethane/pdfs/noreg/109-01836.pdf
[14] http://www.huntsman.com/polyurethanes/Media%20Library/a_MC1CD1F5A7BB1738E040EBCD2B6B01F1/Products_MC1CD1F5AB8081738E040EBCD2B6B01F1/Construction_MC1CD1F5AEF051738E040EBCD2B6B01F1/Technical%20presentati_MC1CD1F5AF6F41738E040EBCD2B6B01F1/files/cpi_08_lifengwu_revised.pdf
[15] Sachchida N, Singh Jody S, Fife Sheila Dubs and Paul D Coleman 2017 Effect of Formulation Parameters on Performance of Polyisocyanurate Laminate Boardstock Insulation Huntsman (Advanced Technology Center, 8600 Gosling Road, The Woodlands, TX 77381)
[16] Gravit M, Gumenyuk V, Sychov M and Nedryshkin O 2015 Procedia Engineering 117 Pp 119-125
[17] Uvarova S, Belyaeva S, Kankhva V, Vlasenko V 2016 *Procedia Engineering*, **165** 1317-1322 https://doi.org/10.1016/j.proeng.2016.11.857
[18] Korolyov and Petrakov G 2010 *Engineering and Construction Journal* **1** C 23-25
[19] Pavlova D 2016 *Comparative analysis of thermal insulation materials in the construction of heat traces* (St. Petersburg: SPbPU) 176s
[20] Tabakova A 2016 *Increase in the efficiency of heating networks as an element of the energy management system of the university* (St. Petersburg: SPbPU) 74c
[21] Belodedov A 2016 *Development and investigation of physical properties of ferritic composite materials* (SPb: SPbPU) 81p.
[22] URL: http://www.nappan.ru/library/eef/features_ppy/.
[23] Akulova M 2011 *Bulletin of MGSU* **3** 65 p.
[24] Cabulis U, Kirpluks M, Stirna U, LopezM J and Vargas Garcia M 2012 *Journal of Cellular Plastics* **48(6)** pp 500-515
[25] Silva M, Takahashi J, Chaussy D, Belgacem M and Silva G 2010 *Journal of Applied Polymer Science* **117** pp 3665-3672
[26] Zatorski W, Brzozowski Z and Kolbrecki A 2008 *Polymer Degradation and Stability* **93(11)** pp 2071-2076
[27] Stirna U, Beverte I, Yakushin V and Cabulis U 2011 *Journal of Cellular Plastics* **47(4)** pp 337-355
[28] Gao L, Zheng G, Zhou Y, Hu L, Feng G and Zhang M 2014 *Polymer Degradation and Stability* **101** Pp 92-101
[29] Feng F and Qian L 2013 *PolymerComposites* **35(2)** pp 301-309
[30] Meng X, Ye L, Zhang X, Tang J, Ji X and Li Z *Journal of Applied Polymer Science* **114(2)** pp 853-863
[31] Paciorek-Sadowska J, Czuprynski B and Liszkowska J 2012 *Casimir the Great University, Bydgoszcz* Pp 302-306
[32] Chattopadhyay D and Webster D 2009 *Progress in Polymer Science* **34** Pp 1068–1133
[33] Volz T and Skowronski M 2009 *Comparison of Blowing Agent Performance in Polyisocyanurate Foams used in the Production of Rigid Faced Continuous Panels (CPI)*
[34] L Montero De Espinosa and Meier M 2011 *European Polymer Journal* **47** pp 837–852
[35] Mosiewicki M and Aranguren M 2013 *European Polymer Journal* **49(6)** pp 1243–1256
[36] Zieleniewska M, Leszczyński M, Kurańska M, Prociak A, Szczepkowski L, Krzyżowska M and Ryszewska J 2015 *Industrial Crops and Products* **74** pp 887–897
[37] Kankhva V, Uvarova S, Belyaeva S 2016 *Procedia Engineering* **165** pp. 1046-1051. https://doi.org/10.1016/j.proeng.2016.11.818
[38] Fire resistance and fire hazard of coating structures based on steel profiled sheet with polymer insulation 2015 FGBU VNIIPo EMERCOM of Russia C 29
[39] URL: https://www.forumhouse.ru/articles/house/6786
[40] URL: http://www.creonenergy.ru/news/post_relizy/detailPost.php?ID=119965
[41] BSEN 14315-1: 2013 Thermal insulation products for buildings - locally produced rigid polyurethane foam (PUR) and polyisocyanurate foam (PIR)
[42] ASTM C1289 − 16a Standard Specification for Faced Rigid Cellular Polyisocyanurate Thermal Insulation Board
[43] ASTM C11029 − 15 Standard Specification for Spray-Applied Rigid Cellular Polyurethane Thermal Insulation