



INVESTIGATION OF THE CONDITIONS OF ALCOHOLIZATION OF SECONDARY POLYETHYLENE TEREPHTHALATE WITH TRIETHANOLAMINE

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Abstract.

Every minute, a million plastic bottles are bought around the world. More than 480 billion plastic bottles were sold around the world in 2016, over the past decade - 300 billion. Today, the search for an efficient way to recycle used food packaging based on polyethylene terephthalate (PET) is one of the environmental problems of the chemical industry. In 2021, the global polyethylene terephthalate (PET) market was 24.23 million metric tons. The PET market size is expected to reach 33.07 million metric tons by 2029, growing at a CAGR of 4.2% during the forecast period from 2022 to 2029.

In many countries around the world, the problem of recycling packaging products based on biodegradable polymers (polyethylene terephthalate bottles, films, disposable cups) is one of the most important tasks of mankind. Recently, the number of landfills for all household waste, including polyethylene terephthalate bottles, films, disposable cups, etc., has increased several times. This also applies to polyethylene terephthalate products that do not corrode or decompose. Their number is growing from year to year. One promising solution to this problem is the synthesis of component A polyol secondary polyethylene terephthalate used in the production of foamed polyurethane using the aminolysis process using polyhydric alcohols.

The objective of this work the study of the triethanolamine-based aminolysis process of secondary polyethylene terephthalate involves the synthesis of an amide-containing oligomer and the possibility of using it as an additional catalyst in the production of polyurethane foam.

This article reactions between secondary PET and triethanolamine were studied. In addition, conditions and properties of products obtained during aminolysis of secondary PET were studied. When secondary PET and triethanolamine react with each other in a 1: 1 ratio, thick polyester polyols are formed, which reduces their applicability in the production of polyurethane foam. Studies have shown that the amine-storing oligomer obtained in a 1: 6 ratio of secondary PET and triethanolamine has a slightly higher liquefaction temperature. A low-viscosity oligomer was obtained by increasing the amount of triethanolamine to a certain extent from the reactants, the obtained oligomer can be used in industry due to its low viscosity. The possibility of using the oligomer obtained with the help of secondary PET and triethanolamine as a catalyst in the production of polyurethane foam was demonstrated.

Key words: triethanolamine, PET, secondary polyethylene terephthalate, Phenolphthalein, polyurethane foam (PPU)

Introduction.

Currently, the production of polyurethane foam (PPU) is an intensively developing industry. Modern production allows the production of monolithic and microcellular, elastic, rigid and semi-rigid polyurethane foam in construction. However, they can be combined with other polymers, metal, wood, textiles, etc. When using PPU, the possibilities of mechanization of

construction work are expanded, the mass of buildings is reduced, and savings on heating are provided. The most developing industry is the production of low-density rigid polyurethane foam for construction purposes, used as thermal insulation and at the same time being a structural material. Currently, the consumption of heat-insulating materials from rigid polyurethane foam has reached 1.36 million tons, including their consumption in building sandwich-panel structures is 37%. The reason for this is that PPU is used for all types of construction (civil, industrial, energy) [1, 2].

The density of polyurethane foam is one of the important parameters in the production of rigid polyurethane foam systems. The denser the polyurethane foam, the stronger it is. In the production of denser polyurethane foam, the consumption of raw materials increases, and, accordingly, the cost of the final product.

During the formation of the foam structure, with the isocyanate component unchanged, the structure and properties of the hydroxyl-containing component are the main parameters that determine the structure and properties of the PPP. Therefore, special attention is paid to the composition and structure of the hydroxyl-containing component [3].

The global consumption of PET has exceeded 13 million tons, of which about 1.5 million tons is consumed exclusively by the packaging sector itself. However, this huge increase in PET consumption has led to the accumulation of a huge amount of waste, the disposal of which is difficult on a day-to-day basis. The review presents in detail the latest developments in the field of chemical processing (glycolysis and aminolysis) of PET. A wide range of used depolymerizing agents, reaction conditions, catalysts, depolymerization products, and their potential applications have been described [4, 5].

It can be seen from these data that various products (flame retardant, flame retardant and crosslinking compounds) can be obtained by using the process of aminolysis of recycled PET, which can be used to obtain polyurethane foams.

Indeed, the disposal of plastic waste is a global problem due to the impact of garbage on the environment and the ecology of the planet. The main share in the total mass of polymeric wastes is occupied by polyethylene terephthalate (PET) [6].

Recently, for environmental and economic reasons, many works have been directed towards the processing of PET. One such work is aminolysis with morpholine, hydrazine and polyamine leading to various reaction products in the form of terephthalic acid diamides. Sodium acetate was used as a catalyst. The resulting product was named bis (2-hydroxyethyl) terephthalamide (BHETA). From the amide obtained by the interaction of 1,4-butanediol and a simple ether polyol with different molar ratios of hexamethylene diisocyanate, a polyurethane with different properties was obtained. The resulting material was used as an adhesive and coated [7, 17].

The study is devoted to the use of ethylene glycol and diethylamine for the aminoglycolytic degradation of polyethylene terephthalate (PET) waste in the presence of xylene. The resulting oligomers had carboxyl, hydroxyl and amine end groups at the end of PET aminoglycolysis. All products were characterized by acid, hydroxyl and amine values, as well as by Fourier transform infrared spectroscopy and differential scanning calorimeter. The resulting products are recommended for use as coatings, such as water-reducible alkyd resins and epoxy resins [8, 15]. In another work, the use of ethylenediamine as a degrading agent also produced amine-containing oligomers. The influence of the ratio of monomers on the yield of bis (2-aminoethanol) terephthalamide was studied [9, 16].

A brief analysis of the literature data shows that the study of the process of aminolysis of secondary polyethylene terephthalate and the production of new products is growing more and more. At the same time, the main emphasis is placed on reducing the cost, modifying fibers,

Obtaining polyurethane foam. PPU was obtained by a single-stage method. To do this, first component A was weighed in a 0.5 l polyethylene cup - a mixture of hydroxyl-containing components with target additives according to one of the recipes, mixed with a disk mixer with a speed of 2800-3000 rpm for 10-30 seconds. Then a pre-weighed amount of component B - polyisocyanate was added, mixed with the same stirrer for 3-5 seconds, and free foaming was observed.

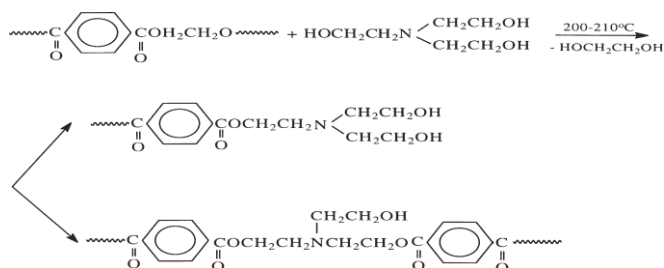
Results and discussion.

Recently, one of the urgent problems has become the processing of waste storage of polyethylene terephthalate (PET), which today accounts for 20-25% of solid and household waste [10]. The number of PET bottles is growing every year, for example, in Russia 2-3 million tons per year, in Uzbekistan 50-80 thousand tons, the complexity of PET waste is that they do not decompose spontaneously in the atmosphere. However, it is destroyed by mechanical processing and temperature.

Over the past 20 years, many scientists have proposed methods for recycling polyethylene terephthalate waste using both physical and chemical processing methods [11]. The most effective of these methods is the chemical method, which results in the production of various hydroxyl-containing polyols [12], unsaturated polyesters, foamed polyurethane catalysts, nitrogen-containing compounds, etc. Allows you to get connections of type. For example, S.V. Porfireva processed PET with TEA and prepared a 10-20% solution, which was used to modify the A-component in the production of polyurethane foam [13]. The results showed that the foam is suitable for polyurethane. V Balaklin demonstrated the possibility of obtaining a flammable nitrogen-containing compound by aminolysis of recycled PET with diamines [14] and found that it can be used in the composition of wood.

Based on the above data, taking into account the recent efficiency of recycled PET in the aminolysis process, our work is to study the process of alcoholization of SPET with triethanolamine and the possibility of using the obtained product as a catalyst in polyurethane foam.

Study of the process of alcoholization of secondary PET with triethanolamine. According to the mechanism of aminolysis, the reaction of secondary PET with triethanolamine can be predicted as follows.



Initially, we studied the effect of the ratio of TEA from 0.5 to 6 mol per mol of the elementary unit taken for synthesis on the physicochemical properties of HPET. The synthesis conditions were taken from the literature data. At the same time, the synthesis temperature is 225°C and the duration is 6 hours.

From the data, with an increase in the amount of TEA from 0.5 to 6 mol, an increase in the content of hydroxyl groups from 459 to 1171.5 mg KOH / g is observed.

In addition, for samples 1:0.5 and 1:1 mol e. unit/mol, the Ubbellod dropping point decreases from 178 to 98°C, respectively. Starting at a ratio of 1:4 the samples become liquid. Analyzing the results of the study, we chose the ratio SPET:TEA = 1:4 mol of an electronic unit / mol and studied the effect of temperature on the properties of products. Temperature range from 200 to 240°C. So published M.M. from 196 to 160, increasing the content of hydroxyl groups and the number of saponification from 577 to 1046 mg KOH / g, 72.8 to 146.4 mg KOH / g.

Accordingly, it should be noted that with an increase in temperature to 240°C, the samples become not fluid, for sure this is due to side reactions with increasing temperature.

Next, we studied the effect of the duration of the aminolysis process with TEA. Thus, the influence of the parameters (temperature, ratio, duration) of the SPET aminolysis process on the physicochemical properties was studied. At the same time, it was found that after the ratio of SPET: TEA = 1:4 mol e.link / mol becomes fluid.

The structures of the synthesized products of alcoholysis are studied by the method of IR - spectroscopy. The structures of the initial and obtained products of alcoholysis were studied by IR spectroscopy in the range from 400 to 3600 cm⁻¹.

On the IR - spectrum of the original PET (Fig. 1) there are transmission bands of methylene groups at 2870, 2932 sm⁻¹, ester groups in the transmission region of 1715 sm⁻¹, at 1580, 1506 bands of transmission of aromatic rings.

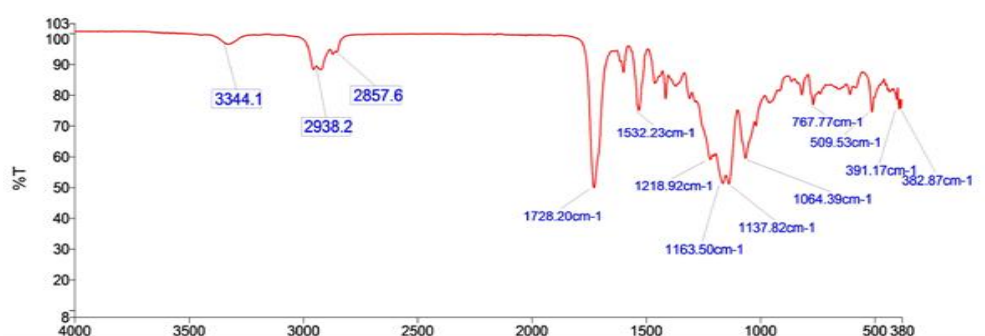


Fig. 1. IR - spectrum of secondary polyethylene terephthalate

And on the IR spectra of triethanolamine there are absorption bands at 3353 sm⁻¹ of primary hydroxyl groups, at 2950 and 2870 sm⁻¹ of methylene groups, bands of absorbed tertamine groups at 1151, 1069, 1037 sm⁻¹.

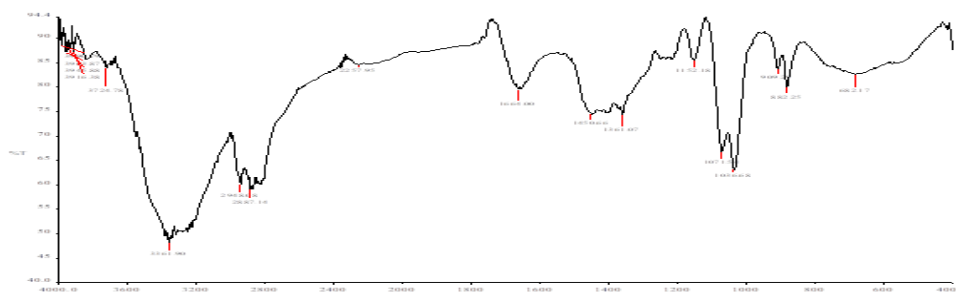


Fig. 2. IR spectrum of triethanolamine.

On the IR spectra of the synthesized aminolysis products (at a ratio of SPET: TEA = 1:0.5 mol e. unit / mol,) there are transmission bands of hydroxyl groups at 3445 sm⁻¹, methylene groups 2957 sm⁻¹, ester groups at 1718 sm⁻¹, aromatic rings at 1555, 1505 cm⁻¹, tertiary amine group 1269 sm⁻¹, primary hydroxyl groups at 1099, 1017 sm⁻¹.

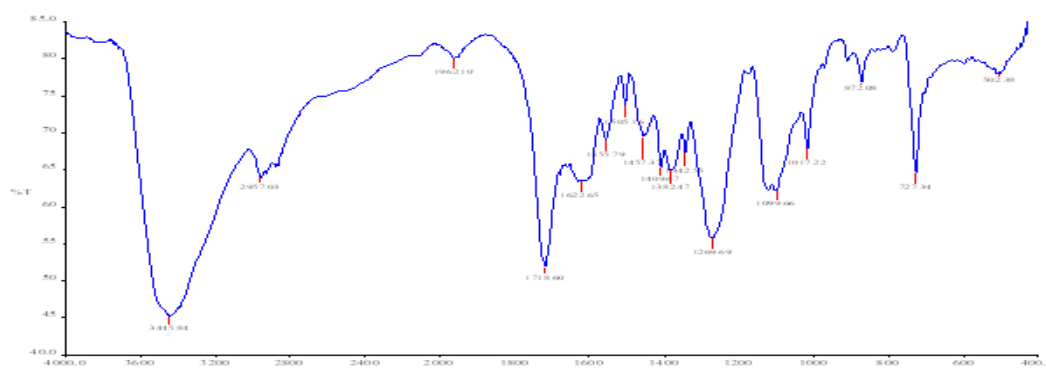


Fig. 3. IR - spectrum of products of aminolysis of secondary PET:TEA =1:0.5 mol el. links per mole.

The presence of tertiary and primary groups in the IR spectra of the synthesized products of alcoholysis indicates the occurrence of exchange reactions due to ester groups.

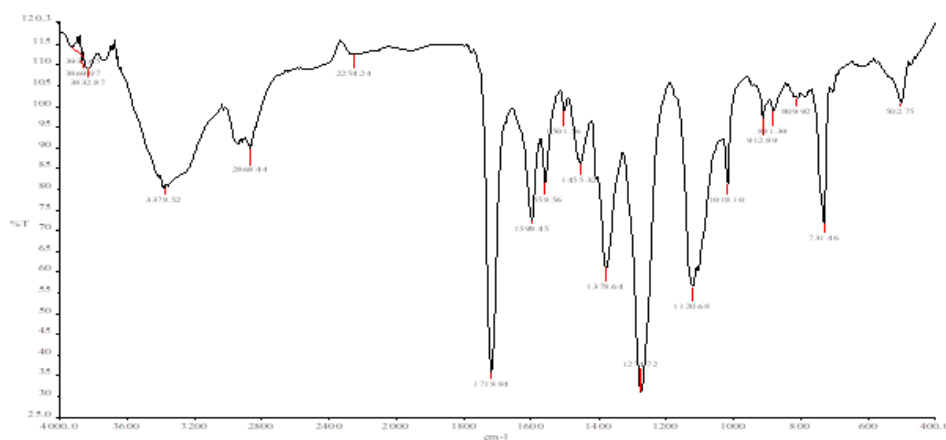


Fig. 4. IR - spectrum of products of aminolysis of secondary PET:TEA 1:1 mol el. links per mole.

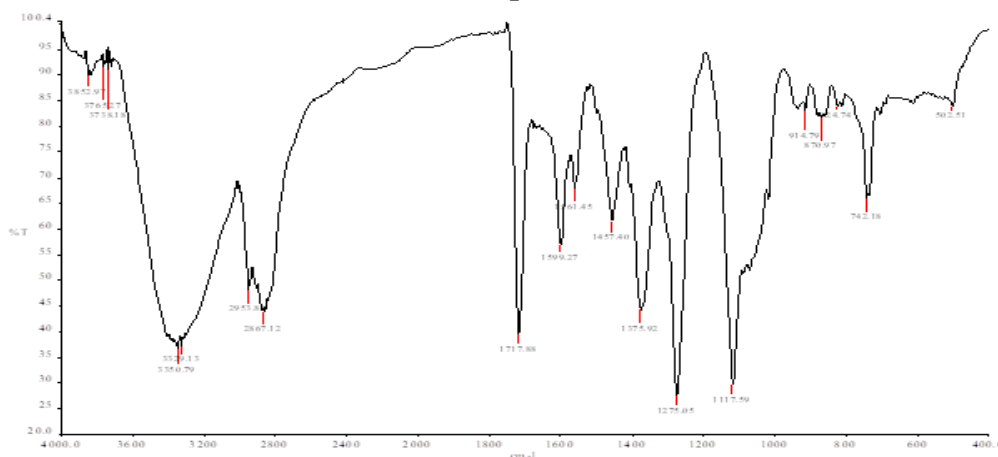


Fig. 5. IR spectrum of products of aminolysis of secondary PET:TEA 1:4 mol el. links per mole.

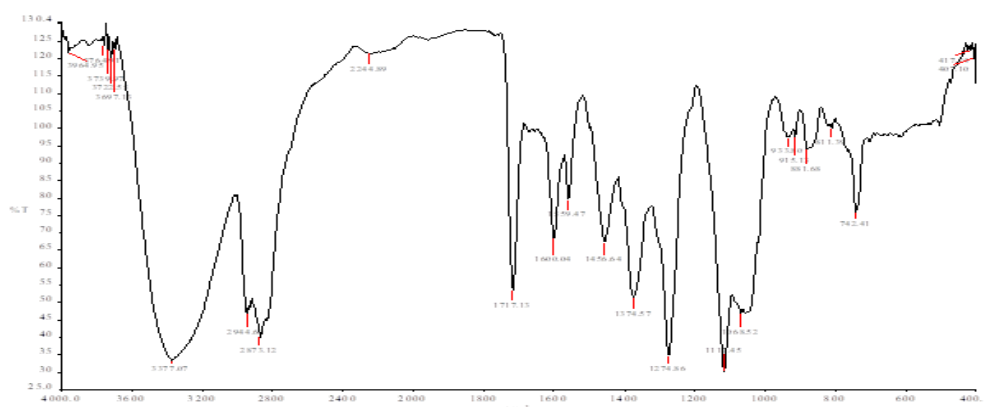


Fig. 6. IR - spectrum of products of aminolysis of secondary PET:TEA 1:6 mol el. links per mole.

The oligomers synthesized at various ratios of SPET:TEA were subsequently used as the main catalyst system in the production of polyurethane foams. The PPU-307 formulation was

used as the base. In addition, with an increase in the amount of the SPET aminolysis product, the apparent density increases from 37.4 to 63.07 kg/m³ (Table 4).

Formulation and technological properties of polyurethane foams based on products of aminolysis of secondary polyethylene terephthalate.

Table 1

Recipe, wt.h.	1	2	3	4	5	6
L-373	95	90	85	80	75	70
L-294	-	-	-	-	-	-
SPET:TEA	5	10	15	20	25	30
H ₂ O	1,5	1,5	1,5	1,5	1,5	1,5
KEP	1	1	1	1	1	1
PIT	18.87	19.72	20.58	21.43	22.28	23.14
Technological properties						
Start time, s	25	18	17	15	12	10
Gel time, s	178	136	99	75	62	41
Rise time, s	243	210	141	121	87	63
Apparent density, kg/m ³	37,4	46,35	53,3	54,5	59,90	63,07
Height (cm)	15	15	14.5	14.5	14	13

The table shows that an increase in the amount of the aminolysis product leads to a decrease in the start time from 25 to 10 seconds, the gelation time from 178 dan to 141 seconds, and the rise time from 243 to 63 seconds. With an increase in the amount of amine-containing oligomer, an increase in fire resistance from 63.4 to 46.16% is observed. And other mechanical properties did not change significantly.

Conclusion

The structure and physical-chemical properties of the obtained products were determined. The process of alcoholization of secondary polyethylene terephthalate with triethanolamine has been studied. The structure of aminohydroxyl-containing oligomers has been studied by chemical and IR spectroscopic methods.

Thus, the conducted studies have shown the possibility of obtaining a nitrogen-hydroxyl-containing oligomer with a wide range of functionalities and properties.

Based on the developed AGSO and used as a catalyst-crosslinking agent, rigid polyurethane foams for a wide range of applications were obtained.

References

1. Международная конференция «Полиуретаны-2012» Полимер. Матер.: изделия, технол. 2012. №4, с. 48-50. РЖХим 12.09-19Т.6
2. Дж. Х. Саундерс, К.К. Фриш «Химия полиуретанов» Москва 1968 г.
3. Игнатъев В.А., Киселева Т.А., Н.И. Кольцов «Синтез и свойства полиуретановых эластомеров на основе сложноэфирных уретановых форполимеров» Уфа. 2012. С. 98-99 РЖХим 13.02-19С.589

4. Neena George and Thomas Kurian. Последние разработки в Переработка отходов полиэтилентерефталата. J: Industrial and engineering chemistry August 28,2014 P-1413-1493 Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 22, Kerala, India.
5. Kazuki Fukushima, Julien M. Lecuyer, Di S. Wei, Hans W. Horn, Gavin J. Jones, Hamid A. Al-Megren, Abdullah M. Alabdulrahman, Fares D. Alsewailem, Melanie A. Mc Neil, Julia E. Rice and James L. Hedrick. Химическое восстановление поли (этиленцефталата) спомощью органокаталитик аминоллиз. Polym. Chem., 2013, 4, 1610.
6. Mangovska B, Bogeva-Gaceva G, Pohlers A (1996) Structure and basic properties of aminated PET. J Appl Polym Sci 62:605– 612
7. A. S. Goje, A. Thakur, V. R. Diware, Y. P. Chauhan, and S. Mishra, *Аминолиз поли (этилен цефталата) отходов для восстановления продуктов с добавленной стоимостью* \\.DOI: 10.1081/PPT-120029971 0360-2559 ,(Print); 1525-6111 (Online) Copyright 2004 by Marcel Dekker, Inc. www.dekker.com 407-426 стр.
8. В.М. Балакин, А.А. Галлямов, Д.Ш. Гарифуллин, К.Д. Абдуллина фосфорсодержащие антипирены для древесины на основе продуктов аминоллиза полиуретанов. \\. фгбоу впо «Уральский государственный лесотехни-ческий университет»; e-mail: balakin_v.m@mail.ru; г. Екатеринбург, ул. Сибирский тракт, 35; кафедра технологии переработки пластмасс; 98-105 стр.
9. Işıl Acar, Ayşe Bal, Gamze Güllü, Влияние ксилола как ароматического растворителя на Аминогликолиз ПЭТ бутылок после потребления. \\. Department of Chemical Engineering, Faculty of Engineering, Istanbul University 34320 Avcılar, Istanbul, Turkey, Correspondence to: Işıl Acar; e-mail: acar@istanbul.edu.tr, Project Number 3368. DOI 10.1002/pen.23491, Published online in Wiley Online Library (wileyonlinelibrary.com). VVC 2013 Society of Plastics Engineers polymer engineering and science—2013, 2430-2438 стр.
10. Пилунов Г.А. Переработка отходов ПЭТФ / Г.А. Пилунов // Химическая промышленность. 2001. № 6. С.22-27.
11. Журавлев А.Б. Пути утилизации бытовых отходов полиэтилентерефталата / А.Б. Журавлев, Р.И. Адилов, М.Г. Алимухамедов, Ф.А. Магруппов // Пластические массы. 2005. №3. С.47-53.
12. Конструкционные материалы на основе полиэтилентерефталата. М.: НИИТЭХИМ, 1991. 48 с
13. Порфирьева С.В. Получение и исследование пенополиуретанов с использованием вторичного полиэтилентерефталата / С.В. Порфирьева, Е.В. Соловьев, Е.Ю. Степанова, В.Г. Петров,
14. В.М. Балакин, М.А. Красильникова. ОГНЕЗАЩИТНЫЕ СОСТАВЫ ДЛЯ ДРЕВЕСИНЫ НА ОСНОВЕ ПРОДУКТОВ АМИНОЛИЗА ПЭТФ ДИАМИНАМИ И ПОЛИАМИНАМИ. 2011
15. Bernal M. Mar, Lopez-Manchado Miguel Angel, Verdejo Raquel. “Усовершенствование in situ вспенивания мягких нанокотпозитных пенополиуретанов. In situ foaming of flexible polyurethane foam nanocomposites”. Macromol. Chem. And Phys. 2011. 212, № 9, с. 971-979. Англ. РЖХ 12.01-19Т.314
16. Pt. II. Borreguero, A. M. Rodriguez Zuan, Valverde Jose Juis, Arevalo Regual, Peijs Ton, Cormana Manuel. J. Mater. Sci. Характеристика жестких пенополиуретанов содержащих микрокапсулированный. // Rubitherm RT 27 Ч. П. Влияние катализатора characterization of rigid polyurethane foams containing microencapsulated. Rubitherm. R. T 27. catalyst effect. 2011. 46 №2. с. 347-356 Англ. РЖХ 11.11-19Т-242
17. Aslzadeh M. M, Mir Mohamad Sadeghi G., Abdouss M. J. Appl “In situ polymerization and characterization of chlorine-containing flame retardant polyurethane compositions. Synthesis and characterization of chlorine-containing flame-retardant polyurethane nanocomposites via in situ polymerization”. Polym. Sci 2012. 123, № 1, с. 437-447. Англ. РЖХ 12.12-19Т. 337.