

Modifications of the Rigid Polyurethane–Polyisocyanurate Foams

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ABSTRACT: The method of boroorganic compounds preparation by esterification of boric acid and glycols has been presented. The obtained compounds tri(2-hydroxybutyl)borate, tri(hydroxythiodiethylene)borate, tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate, and tri[3-chloro-2-hydroxy-1-propoxy]thiodiethyl]borate were used to produce the rigid polyurethane–polyisocyanurate (PUR-PIR) foams. The foams were prepared by one-stage method and the amount of borates added varied, within the range from 0.0 to 0.4 of chemical equivalent. The method of preparation, determination of foaming parameters, and methods of testing of the physicochemical properties of PUR-PIR foams as well as their results have been presented. A special emphasis

was put on reduction of the foam flammability. It was found that application of the obtained compounds as polyolic components has a favorable effect on the properties of the produced rigid PUR-PIR foams. The obtained rigid PUR-PIR foams were characterized by a higher compressive strength, lower brittleness, considerably reduced flammability, and higher content of the closed cells. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2020–2029, 2006

Key words: rigid polyurethane–polyisocyanurate foam; properties of the rigid foams; boron oligomerols; borochlorine oligomerols; flammability of foams; borates

INTRODUCTION

Plastic industry belongs to the most dynamically developing branches of Polish economy, which is generally recognized as a leader of economic transformations in the Middle and the East Europe.¹ Dynamics of this process has been particularly observed during the last years. Production of polyurethanes has a significant effect on the situation mentioned earlier, since their consumption has still an increasing tendency. Greater part of it is produced in the form of rigid polyurethane foams, which are mainly applied as heat insulations in many branches of industry, such as refrigerating and heat engineering.^{2,3}

Polyurethanes can take various forms in respect of the chemical structure of the polymeric chains and the general structure of the polymer. The essential feature of polyurethanes is that modifications of their chemical structure have an effect on their properties that often allows to widen the field of their practical applications.⁴

The present article is a continuation of our studies on preparation of compounds having an effect on the reduction of flammability of the rigid polyurethane–polyisocyanurate (PUR-PIR) foams.^{5–8}

The aim of our studies was to obtain new multihydroxyl compounds containing boron and chlorine, which would reduce flammability and improve physicochemical properties of foams when added to receipt (premix). New compounds were obtained by applying tri(2-hydroxybutyl) and tri(hydroxydiethylene)borates, prepared at Faculty of Chemistry, Technology of Polymers and Ecotechnology of Bydgoszcz Academy. Then, the new compounds were subjected to the suitable reactions with epichlorohydrin, resulting in formation of polyhydroxyl flame retardants containing boron and chlorine i.e., tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl] and tri[3-chloro-2-hydroxy-1-propoxy]thiodiethyl] borates.

EXPERIMENTAL

Characteristics of raw materials

The polyether with trade name Rokopol RF-55 (product of oxypropylation of sorbitol $L_{OH} = 495$ mg KOH/g, produced by NZPO “Rokita,” Brzeg Dolny, Poland)¹ and Ongromat 20–30 (technical polyisocyanate, whose main component is diphenylmethane 4,4'-diisocyanate, made in Hungary) were used to prepare the rigid PUR-PIR foams. The density of Ongromat 20–30 at a temperature of 25°C was 1.23 g/cm³, and its viscosity was ~200 mPa s. The polyisocyanate contained 31.0% of isocyanate (NCO) groups. It was characterized according to the ASTM D 1638–70 standard.

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An anhydrous potassium acetate in the form of 33% solution in diethylene glycol (Catalyst-12, POCh Gliwice, Poland) and amine catalyst in the form of 33% solution of triethyleneamine in dipropylene glycol (DABCO, Hondrt Hüls, Germany) were used in foam composition.

The polysiloxanepolyoxyalyleneoxydimethylene copolymer characterized by the boiling point of 150°C at 1013 hPa and ignition temperature of 90°C (Niax Silicone L 6900, Witco Corp., USA) was used as a surfactant.

The porophor was carbon dioxide formed in situ in reaction of isocyanate with distilled water. Moreover, tri(2-chloro-1-methyl-ethyl) phosphate (Antiblaze, Albright and Wilson, United Kingdom) was introduced into foams.

Tri(2-hydroxybutyl), tri(hydroxythiodiethylene), tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl],

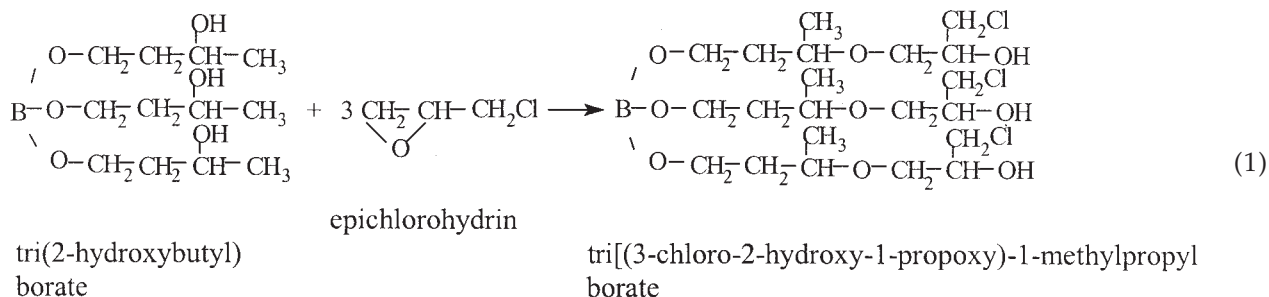
and tri[3-chloro-2-hydroxy-1-propoxy)thiodiethyl]borates obtained from Faculty of Chemistry, Technology of Polymers and Ecotechnology of Bydgoszcz Academy were applied as modifiers for preparation of foams.

Preparation of boroorganic compounds (modifiers)

Preparation of tri(2-hydroxybutyl) and tri(hydroxythiodiethyl)borates was described by Czupryński et al.⁶

Preparation of tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate

Synthesis of oligomerol on the basis of tri(2-hydroxybutyl) borate and epichlorohydrin was conducted according to the following scheme [eq. (1)]:

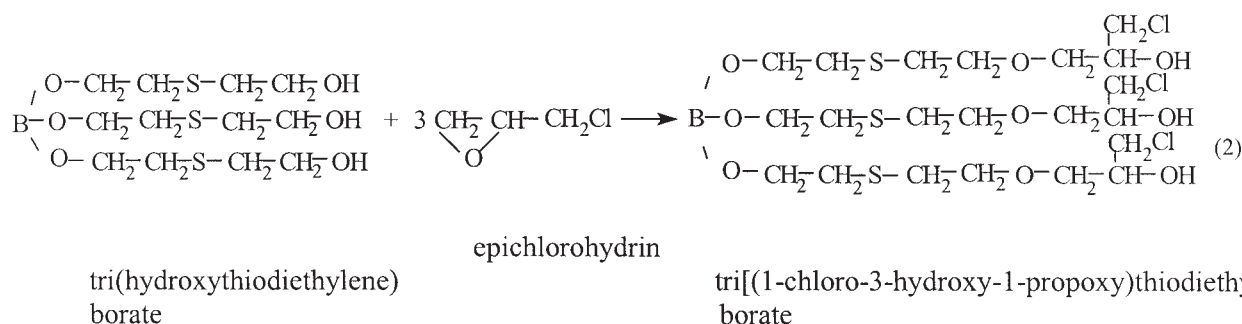


51.6 g (0.2 mol) of tri(2-hydroxybutyl)borate, 55.5 g (0.6 mol) of epichlorohydrin, and 2.68 g of BF_3 were introduced (at temperature of 50°C and with continuous stirring) into a three-necked flask (250 cm³), equipped with a reflux condenser, thermometer, and stirrer. Then, the temperature was risen to 105°C (378K), and the reaction run for 2.5 h. After that time, the temperature was risen to 120°C and reaction run for a consecutive 0.5 h. A clear yellow liquid product was obtained, and its main component was tri[(3-

chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate.

Preparation of tri[(3-chloro-2-hydroxy-1-propoxy)thiodiethyl]borate

Synthesis of oligomerol on the basis of tri(hydroxythiodiethylene)borate and epichlorohydrin was conducted according to the following scheme [eq. (2)]:



74.8 g (0.2 mol) of tri(hydroxythiodiethylene)borate, 55.5 g (0.6 mol) of epichlorohydrin, and 2.68 g of BF_3 were introduced (at a temperature of 50°C (323K) and

with continuous stirring) into a three-necked flask (250 cm³), equipped with a reflux condenser, thermometer, and stirrer. Then, the temperature was risen

TABLE IV
Properties of the Prepared Boroorganic Oligomerols

Boroorganic compound	Properties			
	Hydroxyl number (mg KOH/g)	Density at 20°C (g/mole)	Viscosity at 20°C (mPa s)	pH
Tri(2-hydroxybutyl) borate	423.4	1.1	51.4	4.4
Tri(hydroxythiodiethylene) borate	319	1.5	133.2	4.5
Tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl] borate	300	1.07	60.3	4.2
Tri[(3-chloro-2-hydroxy-1-propoxy)thiodiethyl] borate	259.9	1.33	433.3	4.2

Preparation of the rigid PUR-PIR foams and methods of their evaluation

The prepared boroorganic compounds—after their physicochemical properties had been determined—were applied to prepare the rigid PUR-PIR foams. Compositions of the rigid PUR-PIR foams are given in Tables V and VI.

The rigid PUR-PIR foams were produced, according to the receipts mentioned earlier, in such a manner, that the weighted amount of polyisocyanate was introduced into one polypropylene vessel (1 dcm³), and the oligomerol with auxiliary substances were put into another one. Oligomerol was thoroughly mixed with all the components using electric stirrer (1800 rpm).

Polyisocyanate was merged with polyol component and stirred thoroughly for about 15 s. Then, it was poured into a form and expanding of foam was observed. An open form was applied, in our studies, to allow the foam to expand freely. The form was made of steel (3 mm) and its internal dimensions were 25×25×30 cm³.

During synthesis of PUR-PIR foams, the course of the reaction mixture foaming was monitored by measuring the respective production times i.e., start, expanding, and gelation times.

Start time: It is the time, measured by a timer, from the moment when all the components were mixed to

the moment when the so-called “creamy state” was attained. It was visualized by the beginning of the foam expansion.

Time of expanding: It is the time, measured by a timer, from the moment when all the components were mixed to the moment when the foam attained maximum volume.

Gelation time: It is the time, measured by a timer, from the moment when all the components were mixed to the moment when free surface of foam ceased to stick to a clean glass rod.

The foams were denoted by the symbols: (S, Standard), a foam with no borate added; (B1–B4), foams containing tri(2-hydroxybutyl)borate; (EB1–EB4), foams containing tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate; (EH1–EH4), foams containing tri[(3-chloro-2-hydroxy-1-propoxy)butyl]borate; (T1–T4), foams containing tri(hydroxythiodiethylene)borate; and (ET1–ET4), foams containing tri[(3-chloro-2-hydroxy-1-propoxy)thiodiethyl]borate.

The expanded foams, after they had been removed from the form, were thermostated for 4 h at a temperature of 423 K.

Then, the foams were cut to samples of dimensions suitable for the individual tests, and their properties were determined according to the obligatory standards.

TABLE V
Compositions of the Rigid PUR-PIR Foams Using Borate Obtained from Boric Acid and 1,3-Butanediol

	H1	H2	H3	H4	EH1	EH2	EH3	EH4
Rokopol RF-55	0.9 (50.99) ^a	0.8 (45.32)	0.7 (39.66)	0.6 (33.9)	0.9 (50.99)	0.8 (45.32)	0.7 (39.66)	0.6 (33.9)
Tri(hydroxybutyl) borate	0.1 (3.15)	0.2 (6.3)	0.3 (9.45)	0.4 (12.61)				
Tri[(3-chloro-2-hydroxy-1-propoxy)butyl] borate					0.1 (4.26)	0.2 (8.53)	0.3 (12.79)	0.4 (17.05)
Silikon L6900	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
DABCO	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Catalyst 12	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Antiblaze TMCP	46.1	46.1	46.1	46.1	46.1	46.1	46.1	46.1
Water	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)
Ongromat 30–20	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)

^a Values given are chemical equivalents; values in parentheses are given in grams.

TABLE VI
Compositions of the Rigid PUR-PIR Foams Using Borates Obtained from Boric Acid and Thiodiethylene Glycol

	T1	T2	T3	T4	ET1	ET2	ET3	ET4
Rokopol RF-55	0.9 (50.99) ^a	0.8 (45.32)	0.7 (39.66)	0.6 (33.9)	0.9 (50.99)	0.8 (45.32)	0.7 (39.66)	0.6 (33.9)
Tri(hydroxythiodiethylene) borate	0.1 (6.69)	0.2 (13.39)	0.3 (20.08)	0.4 (26.78)				
Tri[(3-chloro-2-hydroxy-1-propoxy) thiodiethyl] borate					0.1 (7.79)	0.2 (15.58)	0.3 (23.37)	0.4 (31.16)
Silikon L6900	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
DABCO	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Catalyst 12	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Antiblaze TMCP	46.1	46.1	46.1	46.1	46.1	46.1	46.1	46.1
Water	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)	0.7 (3.15)
Ongromat 30–20	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)	3.7 (250.1)

^a Values given are chemical equivalents; values in parentheses are given in grams.

Brittleness of foams was determined using standard apparatus, according to ASTM C 421–61 standard. It was calculated as a mass decrement (in percents) of 12 foam cubes (side of 25 mm) in relation to their initial mass. Apparatus applied to determine the brittleness of PUR foams was a cubical box (190 × 197 × 197 mm³), made from an oaken wood and rotating about an axis with a speed of 60 rpm. The box was filled with 24 oak cubes (20 × 20 × 20 mm³).

An apparent density of foams was determined by using the cubical samples (side of 50 mm, ISO 845:1988 standard) as a ratio of foam mass to its geometric volume.

Change of the linear dimensions, volume, and mass decrement of foams were determined after 48 h of thermostating at a temperature of 120°C (393K) by using the cubical samples (side of 50 mm). Samples were measured longwise the direction of the foam expansion.

Softening point—as a thermal resistance under compressive stress—was determined by using the cubical samples (side of 20 mm), longwise the direction of foam expansion, in accordance with DIN 53424 standard. The foam samples were subjected to a compressive load of 24.52 kPa/h at a temperature of 50°C. The temperature at which compression of sample by 2 mm occurred was accepted as the softening point.

Thermal conductivity of foams was defined by determination of the thermal conductance, λ . The dimensions of the foam samples were 200 × 200 × 25 mm³, and the investigations were carried out by using “FOX 200” apparatus (Lasercomp). It allowed us to determine λ value within the range from 20 to 100 mW/m K. The necessary condition to take the measurements was a complete filling of the testing chamber.

Content of the closed cells was determined in accordance to PN-ISO 4590:1994 standard by method II (dimensions of samples: 100 × 30 × 30 mm³). The method consisted in determination of the relative pressure drop (earlier calibrated for the volume standards) from the

differences in indications on the scale of manometer whose one arm was opened to atmosphere.

Determination of water absorbability was carried out according to DIN 53433 standard. The method consisted of measurement of the buoyant force of a sample (150 × 150 × 25 mm³) immersed in distilled water for 24 h.

The flammability of the obtained PUR-PIR foams was tested by two methods:

1. According to PN-78 C-05012 standard—horizontal test. The method consisted of determination of velocity of the superficial propagation of flame on the sample (150 × 50 × 13 mm³) placed horizontally and kindled on one end. The tested foam sample was placed on a horizontally fixed net, and then, the burner with a flame was put to one of the ends for 60 s. A transverse line was marked at a distance of 125 mm from the sample end to which the burner was applied. The distance to which the front of flame was shifted and the time required to reach the marked transverse line by the front of flame was measured. If the ignited foam goes out before a control mark is reached by a flame, then the foam is defined as self-extinguishing one.
2. According to ASTM D 3014–73 standard—simplified chimney test—(Butler’s vertical test). Six foam samples (150 × 19 × 19 mm³) were tested. Before burning, the samples were weighted accurate to 0.0001 mm, and then, they were placed inside a chimney. A pane was installed and a flame from the burner, supplied with propane–butane gas, was brought into contact with the sample for 10 s. Then, the burner was removed, and the time of the sample-free burning and retention (residue after burning) were measured by stopwatch in vertical test. Retention was calculated according to the eq. (3):

$$R(\%) = \frac{m}{m_0} \times 100 \quad (3)$$

where R is the retention, m_0 is the mass of the sample before burning [g], and m is the mass of the sample after burning [g].

RESULTS AND DISCUSSION

After the physicochemical properties of the prepared boroorganic compounds had been tested, they were applied to produce the rigid polyurethane.

The industrial oligomerol (Rokopol RF-55) was progressively replaced by the prepared boroorganic compounds, and the rigid PUR-PIR foams characterized by the properties presented in Figures 1, 2, and 3 were obtained. The variables of foam processing were measured during foaming. It was found that the measured times were longer as the content of borates in composition was increased from 0.1 to 0.4 of chemical equivalent (ch. eq.), in comparison to the standard foam (S, with no borate added). Start time of the prepared foams increased from 15 s for standard foam (S) to 30 s for B4 (containing 0.4 of ch. eq. of tri(2-hydroxybutyl)borate and EB4 (containing 0.4 of ch. eq. of tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate. Time of expanding increased from 18 s for S foam to 69 s for ET4 foam (containing 0.4 of ch. eq. of tri[(3-chloro-2-hydroxy-1-propoxy)thiodiethyl]borate, whereas gelation time increased from 35 s for S foam to 95 s for EB4 foam.

Introduction of borates into foam composition in amounts within the range from 0.1 to 0.4 of ch. eq. at the cost of the same quantity of chemical equivalent of Rokopol RF-55 changed their apparent densities in comparison with standard foam (36.96 kg/m^3) e.g., 56 kg/m^3 for ET4 foam.

Changes of linear dimensions, volume, and mass decrement after 48 h of thermostating at a temperature of 120°C were practically analogous. Time of thermostating (48 h) was determined on the basis of experiments carried out earlier. These factors allowed us to state that the most significant changes in foam volume occur between 24 and 72 h of foam ageing.⁹ The type and amount of the applied compounds containing boron and chlorine have no effect on changes of the linear dimensions, volume, and mass decrement of foams being in the sphere of experiments.

The boroorganic compounds applied to produce rigid PUR-PIR foams behave in foam composition similarly to the common crosslinking agents, causing the foam structure to become more ordered. Therefore, on the basis of the brittleness determinations, it was found that addition of boroorganic compounds to foam composition caused reduction of the foam brittleness. For the standard foam, it was equal to 36.2%.

Addition of a compound containing boron caused reduction of brittleness from 9.1% for ET4 foam to 5.43% for B4 foam (containing 0.4 of ch. eq. of tri(hydroxybutyl)borate).

As part of the industrial oligomerol (Rokopol RF-55) was replaced by the obtained boroorganic compounds, the increase in compressive strength of foams was observed i.e., from 365.5 kPa for standard foam to 447.9 kPa for ET4 foam. Increasing the amount of tri(hydroxythiodiethylene)borate in foam composition resulted in a decrease of compressive strength. It was found that the mechanical compressive strength of the produced foams increased as the quantity of chemical equivalent of boroorganic compounds was increased; however, it decreased as the chain of compounds was longer.

Analysis of the softening points of the obtained foams showed that they were slightly lower in the case of foams containing boroorganic compounds i.e., 177°C for standard foam, while 170°C for foams containing 0.4 of ch. eq. of tri(hydroxybutyl)borate. Addition of borochlorine compounds to the foam composition caused increase of softening point to 198°C for foams containing 0.1 of ch. eq. of borate (EB1). However, softening point decreased as the quantity of the chemical equivalent of borochlorine compound was increased in foam composition.

Boroorganic compound added to the rigid PUR-PIR foams caused the decrease of water absorptivity by foams. It was equal to 1.8% v/v for standard foam and for the other foams it decreased to $\sim 0.87\%$ v/v.

Addition of borates for preparation of PUR-PIR foams resulted in a significant increase of the closed cells in comparison with the standard foam. The content of the closed cells varied between 83.4% for standard foam and 97% for foams containing 0.4 of ch. eq. of tri[(3-chloro-2-hydroxy-1-propoxy)thiodiethyl] borate. Application of boroorganic compounds allowed us to produce the foams containing over 90% of the closed cells. Thermal resistance was within the range from 34 to 35 mV/(m K) for all the foams prepared, and there was no strict correlation with content of closed pores in foams. Studies on foams foamed by carbon dioxide, formed in the reaction of polyisocyanates with water, have been carried out for several years.¹⁰ They proved that water—as foaming agent applied to produce the foams—caused a significant increase of the thermal resistance (30 mV/(m K)). For comparison, the thermal resistance of foams foamed by cyclopentane is equal to 20 mV/(m K). Carbon dioxide is a prevalent blowing agent used by foam producers, who have no special requirements concerning thermal conductivity e.g., foams applied in constructions.

Analysis of the flammability test of the obtained PUR-PIR foams showed that the residue after burning (retention) increased as the content of boroorganic

TABLE VII
Physicochemical Properties of the Prepared Rigid PUR-PIR Foams

Symbol of foam	Brittleness (%)	Compressive stress (k Pa)	Content of closed pores (% v/v)	Thermal conductivity (mV/m K)	Softening point (°C)	Absorptivity of water (% v/v)
Standard	36.2	237.5	83.4	35.13	230	1.8
B1	37.1	238.1	91.6	35.01	210	0.93
B2	33.35	251.9	91.7	35.09	198	0.94
B3	20.09	257.8	90.8	34.9	190	0.91
B4	19.04	262.1	92.1	35.07	184	0.89
EB1	15.94	242.2	92.3	35.89	198	0.73
EB2	14.84	269.8	92.7	35.76	188	0.70
EB3	13.66	312.5	91.9	35.91	179	0.76
EB4	11.19	374.8	92.6	35.61	161	0.73
T1	21.4	254.3	93.1	34.70	205	0.91
T2	20.6	295.0	92.2	34.50	200	0.90
T3	15.1	307.3	92.1	34.47	186	0.93
T4	10.2	319.7	90.6	34.72	180	0.92
ET1	14.6	321.5	92.1	35.42	175	0.89
ET2	11.2	369.1	93.7	34.98	170	0.87
ET3	9.8	397.9	93.5	34.79	161	0.90
ET4	9.1	447.9	94.5	35.38	152	0.86

oligomerol was increased in foams containing the same type of oligomerol. The retention values were within the range from 76.59% for standard foam to 96.7% for foams containing 0.4 of ch. eq. of tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate. Retention of foams containing borochlorine compounds was higher than retention of foams containing boron compound only. It was confirmed that chlorine acted as a flame retardant, and this property was intensified by the presence of boron in foam structure. Time of burning was within the range from 10 s for foams containing tri(2-hydroxybutyl)borate to 15 s for foams containing tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate. All the foams obtained are self-distinguishing; however, the foam containing tri[(3-chloro-2-hydroxy-1-propoxy)thiodiethyl]borate is characterized by the shortest burned segment (8 mm). For comparison, the length of the burned segment of the standard foam was 37 mm. The kindled foams were partly burned forming a carbonized protective layer on the surface of sample in the place where the flame was applied. It was observed that, in spite of the various results concerning the range of flame, the flame disappeared when the burner was removed. Therefore, the obtained foams were defined as self-distinguishing. When carrying out the studies on the flammability of rigid PUR-PIR foams, it should be remembered that flammability tests are burdened with a certain error. The error is caused by a susceptibility of tests to any swirl of nascent air during testing. The swirls of air are formed as a result of opening or closing the door of the room or when the burner is quickly removed from the sample. All the described physicochemical properties of foams are presented in Tables VII and VIII.

To confirm the presence of groups typical for foams, the foams were grinded in Iantzki's mill, and then, IR analysis was carried out by potassium bromide technique. The results are presented in Table IX.

IR analysis showed the presence of bands corresponding to urethane group and isocyanurate ring, and it proved that the prepared foams were PUR-PIR ones.

To obtain complete characteristics of the thermal resistance, all the prepared foams were subjected to thermogravimetric analysis in an atmosphere of air, at

TABLE VIII
Flammability Tests of the Prepared Rigid PUR-PIR Foams^a

Symbol of foam	Retention (%)	Time of burning (s)	Reach of flame (mm)	Rate of burning (mm/s)
Standard	78.7	3	37	12.3
B1	84.7	19	31	1.6
B2	90.2	19	20	1.1
B3	92.3	17	18	1.1
B4	93.9	16	17	1.1
EB1	85.2	0	20	—
EB2	89.2	0	19	—
EB3	93.5	0	20	—
EB4	96.7	0	15	—
T1	86.1	11	29	2.6
T2	86.8	10	28	2.8
T3	88.4	10	27	2.7
T4	90.9	9	27	3
ET1	90.4	0	11	—
ET2	92.5	0	10	—
ET3	92.8	0	11	—
ET4	93.3	0	9	—

^a Test definition: self-extinguishing for all foams studied.

TABLE IX
Analysis of IR Spectra of Foams Obtained

Vibration band	ν [cm^{-1}]
Isocyanurate ring	1412–1413 1715–1716
–C=O in urethane	1715–1716
–OH	3296–3306
C–H–CH ₂	2906–2912
–N=C=N–	2136–2139
C–O	1308–1310
C–O–C	1227–1229
C–OH	1067–1075

^a Experimental.

a heating rate of 5°C/min, and within the range of temperature from 20 to 800°C. The first mass decrement, the extrapolated beginning of the first mass decrement, and the highest rate of mass decrement were determined in foams. The first mass decrement occurred at temperature within the range from 195°C for B1 foam to 215°C for ET3 foam. Extrapolated beginning of the main mass decrement occurred within the range of temperatures from 218°C for EB3 foam to 249°C for ET2 foam. However, the highest rate of mass decrement was observed within the range of temperatures from 308°C for EB3 foam to 349°C for T4 foam.

Summary

In reaction of boric acid, epichlorohydrin, 1,3-butane-diol, and thiodiethanediol, the boroorganic and boro-

chlorine compounds—which were not described in literature before—were obtained. Then, they were applied to produce the rigid PUR-PIR foams.

Boroorganic and borochlorine compounds were prepared under laboratory conditions with application of catalysts. All the obtained compounds were analyzed, and then, they were used to produce the foams.

The rigid PUR-PIR foams, with addition of the obtained compounds containing boron, as well as boron and chlorine were prepared by one-stage method at the ratio of NCO to OH group equal to 3:1. It was found that application of the obtained compounds had an effect on elongation of start time and even to the higher degree on the times of expansion and gelation. Application of borochlorine compounds to produce PUR-PIR foams caused increase of the foam density in comparison to the standard foam and moreover an increase of their compressive strength (Fig. 1).

It was found that addition of boroorganic compounds into a foam composition caused decrease of water absorptivity by foams; however, the amount of the closed cells increased significantly in comparison to the standard foam.

On the basis of the results obtained, it was found that foams prepared with addition of compounds containing boron as well as boron and chlorine were characterized by reduced brittleness. Brittleness of foams was decreased as the amount of the earlier mentioned compounds was increased in foam composition (Fig. 2). The

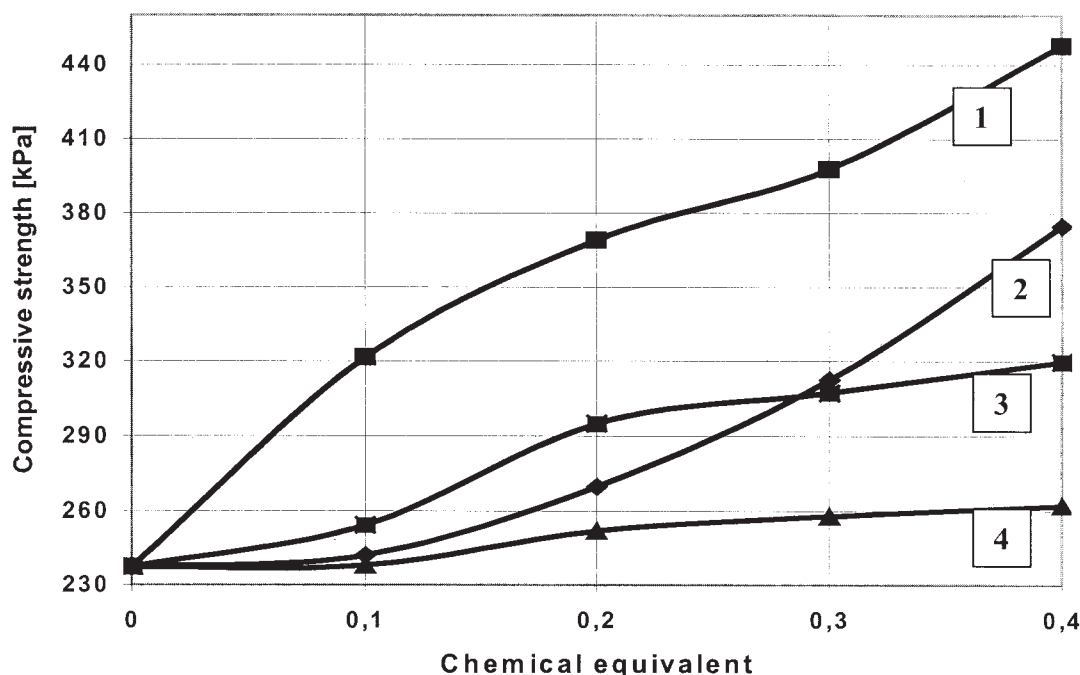


Figure 1 Dependence between compressive strength and content of borates in foams. [1] ET, foam containing tri[(3-chloro-2-hydroxy-1-propoxy)-1-thiodiethyl borate]. [2] EB, foam containing tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate. [3] T, foam containing tri(hydroxythiodiethyl)borate. [4] B, foam containing tri(2-hydroxybutyl)borate.

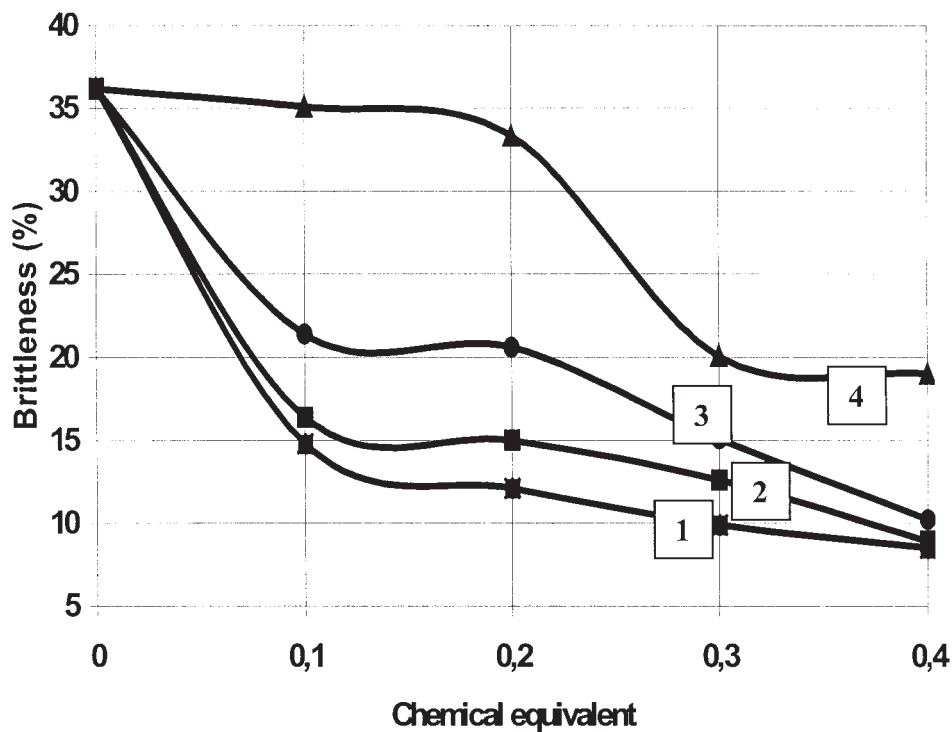


Figure 2. Dependence between brittleness and content of borates in foams. **1** ET, foam containing tri[(3-chloro-2-hydroxy-1-propoxy)-1-thiodiethyl]borate. **2** EB, foam containing tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate. **3** T, foam containing tri(hydroxythiodiethyl)borate. **4** B, foam containing tri(2-hydroxybutyl)borate.

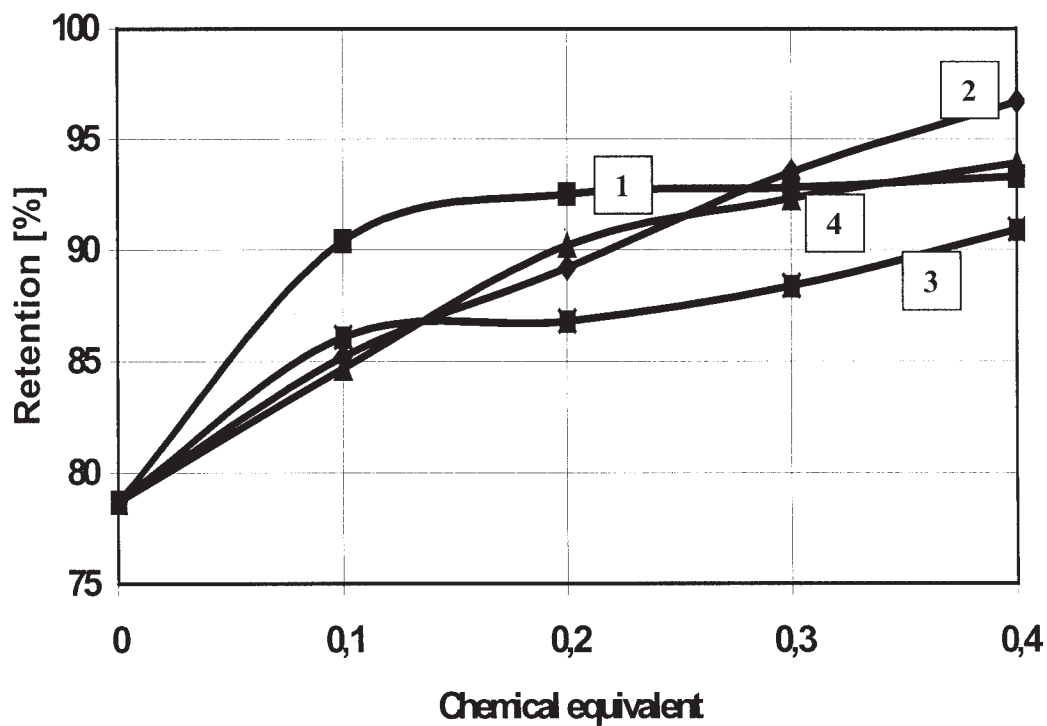


Figure 3. Dependence between retention and content of borates in foam. **1** ET, foam containing tri[(3-chloro-2-hydroxy-1-propoxy)-1-thiodiethyl]borate. **2** EB, foam containing tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylpropyl]borate. **3** T, foam containing tri(hydroxythiodiethyl)borate. **4** B, foam containing tri(2-hydroxybutyl)borate.

lowest value of brittleness was obtained for foams containing tri(hydroxybutyl)borate i.e., below 6%.

The decrease of the softening point was observed as the amount of the obtained compounds was increased in foam composition.

The analysis of the flammability tests of foams allowed us to qualify them to the group of self-extinguishing foams. The maximum reduction of foam flammability (the highest retention) was obtained for foams containing borochlorine compounds (Fig. 3). Increasing the amount of the added new compounds has a favorable effect on reduction of the foam flammability. It was found that foams of higher density (borochlorine) were characterized by a larger after-burning residue.

The majority of PUR-PIR foams produced with addition of compounds containing boron as well as boron and chlorine were characterized by better functional properties than does the standard foam. It should be particularly emphasized that the developed and described foam receipts guarantee preparation of PUR-PIR foams, characterized by compressive strength of about 400 kPa, considerably reduced flammability and brittleness, as well as a high content of the closed cells.

The basic effect achieved by application of the developed method for production of foams are as follows:

- More favorable mechanical properties of foams and especially higher compressive strength, lower brittleness, higher content of the closed cells, and lower absorptivity of water in comparison with standard foam.
- A significant reduction of foam flammability.

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