ISSN 1070-4272, Russian Journal of Applied Chemistry, 2016, Vol. 89, No. 1, pp. 132−139. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © L.K. Sal'keeva, A.A. Bakibaev, G.T. Khasenova, Ye.K. Taishibekova, L.M. Sugralina, Ye.V. Minaeva, A.K. Sal'keeva, 2016, published in Zhurnal Prikladnoi Khimii, 2016, Vol. 89, No. 1, pp. 103−111.

MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Effect of Glycoluril and Its Derivatives on the Flame Resistance and Physico-Mechanical Properties of Rubber

L. K. Sal'keeva[a], A. A. Bakibaev[b], G. T. Khasenova[b], Ye. K. Taishibekova[b], L. M. Sugralina[b], Ye. V. Minaeva[c], and A. K. Sal'keeva[b]

[a] *Buketov State University, ul. Universitetskaya 28, Karaganda, 470074 Kazakhstan*
[b] *National Research Tomsk State University, pr. Lenina 36, Tomsk, 634050 Russia*
[c] *Karaganda State Technical University, bul. Mira 56, Karaganda, 100027 Kazakhstan*
e-mail: LSalkeeva@mail.ru

Received November 24, 2015

Abstract—The effect of bicyclic bisureas (glycolurils) and their derivatives functionalized with hydroxymethyl, halomethyl, and dimethoxyphoshorylmethyl groups on the flame resistance and physico-chemical properties of synthetic isoprene and divinyl rubbers was studied, and the procedures for preparing these agents were suggested. The rubbers with the addition of the synthesized bicyclic bisureas demonstrated satisfactory levels of flame resistance and physico-mechanical parameters.

DOI: 10.1134/S1070427216010213

Imparting flame resistance to materials of various kinds, intended for various purposes, remains a topical problem for a long period. Its urgency is caused by the fact that many materials are sources of serious hazards in cases of fire, being readily ignitable, favoring flame propagation, and releasing large amounts of toxic gases.

Fire retardants reducing the combustibility of rubbers are known for a long time and are efficiently used today. The mechanisms of the action of separate substances and the synergistic effect of their combinations have been interpreted [1, 2]. However, because of the diversity of rubber grades and of ingredients and formulations of rubber stocks, direct application of the available data is impossible, and the performance of specific fire retardants should be evaluated experimentally in each specific case.

A promising line in the development of flame-resistant rubbers is introduction into elastomer compounds of intumescent environmentally safe fireproofing additives. Their properties depend on the atomic ratio of carbon, nitrogen, and phosphorus in their composition [3, 4]. The action of these substances is based on carbonization of the surface of the burning material as a result of their decomposition.

It is known that phosphorus-containing fireproofing agents transform in the course of thermal degradation into (poly)phosphoric acid, which catalyzes the dehydration of the polymeric substrate and leads to its carbonization [3, 5].

EXPERIMENTAL

The structure and properties of the synthesized bicyclic bisurea derivatives were proved by IR and NMR spectroscopy, mass spectrometry, and elemental analysis.

The NMR spectra were recorded with Bruker DRX-300 (operating frequency 300 MHz) and Jeol ECX-400 (operating frequency 400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometers relative to internal HMDS or TMS in DMSO-d_6, $CDCl_3$, or D_2O [accuracy ±(0.1–0.2) ppm]. The mass spectra were taken with a Varian Saturn 2000K device.

The IR spectra were recorded with an FSM-1201 Fourier spectrometer in the range from 450 to 4000 cm^{-1} with 2 cm^{-1} and single scanning (measurement uncertainty ±0.2 cm^{-1}). The samples were prepared as KBr pellets.

The melting points were determined with Boetius (measurement uncertainty ±0.1°) and MP50 Melting Point System devices.

The reaction progress and product purity were monitored by thin-layer chromatography on standard Silufol UV-254 plates. The chromatograms were visualized with iodine vapor or UV lamp.

2,4,6,8-Tetraazabicyclo[3.3.0]octane-3,7-dione (glycoluril) (1). To 60 g (1.0 mol) of urea and 60 g of water, 5.4 mL (0.1 mol) of concentrated sulfuric acid (d = 1.840) and 58 g of a 40% aqueous glyoxal solution (0.4 mol) were added with stirring. The mixture was heated to boil and boiled for 20 min. The reaction mixture was cooled to room temperature, and the precipitate was filtered off, washed with 60 mL of water, and dried. White crystalline powder was obtained. Yield of **1** 48.4 g (85%), mp 360°C. IR spectrum (KBr), ν, cm^{-1}: 3209 (NH), 1675 (C=O). ^{1}H NMR spectrum (400 MHz, DMSO), δ, ppm: 5.20 s (2H, CH), 7.13 s (4H, NH).

2,4,6,8-Tetramethylol-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (2). A suspension of 28.4 g (0.2 mol) of glycoluril **1** and 80 g of 40% formaldehyde solution was alkalized with a 20% NaOH solution to pH 9–10, after which the mixture was stirred at 50°C for 2 h. 70% of water was distilled off, and tetra-*N*-hydroxymethylglycoluril was separated and washed with acetone. Yield of **2** 26.2 g (50%), mp 136.5°C. IR spectrum (KBr), ν, cm^{-1}: 1718.31 (C=O), 3337.39 (OH). ^{1}H NMR spectrum (400 MHz, DMSO), δ, ppm: 5.47 s (2H, CH), 4.62–4.79 m (8H, CH_2).

2,6-Di(chloromethyl)-4,8-dihydroxy-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (3). To 2.0 g (0.0076 mol) of **2** in acetonitrile, 8.4 g (0.0608 mol) of phosphorus trichloride was added at 0–10°C. After that, the mixture was stirred at 70–80°C for 24 h, and the precipitate was filtered off and washed with acetonitrile. Yield of **3** 1.89 g (60.96%), mp 180°C. ^{1}H NMR spectrum (400 MHz, DMSO), δ, ppm: 5.48 s (2H, CH), 7.12–7.23 m (4H, CH_2Cl), 4.65–4.76 m (4H, CH_2OH).

2,6-Di(bromomethyl)-4,8-dihydroxy-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (4). To 3.5 g (0.013 mol) of **2** in toluene, 18.08 g (0.06 mol) of phosphorus tribromide was added. The mixture was heated at 60–90°C for 24 h. The resulting precipitate was filtered off and washed with diethyl ether. Yield of **4** 3.5 g (62.5%), mp 160°C. ^{1}H NMR spectrum (400 MHz, DMSO), δ, ppm: 5.46 s (2H, CH), 7.14–7.21 m (4H, CH_2Br), 4.67–4.73 m (4H, CH_2OH).

Table 1. Physico-mechanical parameters of TG rubbers for external cover layers

Parameter	Prescribed for TG grade rubbers
Nominal tensile strength, MPa	≥14.7
Relative elongation at break, %	≥350
Abrasion loss, mm^3	≤200
Shore hardness A, units	55–70

Phosphorylated derivatives of *tetra-N*-methylolglycoluril (5) and (6). To 2.62 g (0.01 mol) of **2** and 1.58 g (0.02 mol) of pyridine in benzene, 2.89 g (0.02 mol) of dimethyl phosphorochloridate was added at 0°C. The mixture was heated at 60–70°C for 24 h. The reaction progress was constantly monitored by TLC. The precipitate was filtered off and washed with acetone. Yield of **5**, **6** 2.0 g (50.25%). ^{1}H NMR spectrum (400 MHz, DMSO), δ, ppm: 3.16 s [12H, $2P(OCH_3)_2$], 4.34 s [4H, $2CH_2P(O)$], 4.52–4.62 m (4H, $2CH_2$–OH), 5.64 s (2H, CHCH), 3.21 s [6H, $2P(O)OCH_3$], 2.51–2.53 m [8H, $2P(CH_2)_2$]. In the ^{31}P NMR spectrum, there are two signals at 1.0 [$(CH_2)_2P(O)OCH_3$] and 4.0 ppm [$CH_2P(O)(OCH_3)_2$]. However, we failed to separate these products because of their affinity for the solvents.

The formulation for a polymeric compound of decreased combustibility is sought for empirically for each specific article, and the suitability of one or another fireproofing agent as fire retardant can be judged only from the experimental data.

To bring the developed formulations into industrial practice, it is necessary that the rubber obtained should fully meet all the requirements, exhibit improved physico-mechanical properties, and be sufficiently cheap in production. Therefore, it is necessary to consider all the regulations concerning difficultly combustible TG rubber for mines (Tables 1 and 2). TG belts are intended for underground operation at ore-mining enterprises and coal mines with dist and gas hazard at ambient air temperature of –25 to +60°C and humidity of up to 98%.

The rubber stocks under consideration included the following components: rubbers, zinc white, P-324 carbon black, sulfur, sulfenamide Ts, magnesium oxide, zinc stearate, Naftam, Diafen, and nitrosodiphenylamine. The rubber stocks were prepared on rollers and vulcanized in a press.

Table 2. Physico-mechanical and fireproofing characteristics of TG grade rubbers

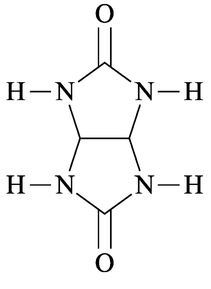
Parameter	Prescribed value	Actual value
Adhesion strength, N mm^{-1}		
between cover layer and carcass	≥6.0	8.0–9.0
between cover layer and breaker	≥6.0	8.0–9.0
between plies	≥6.5	8.0–10.0
between cover layer and thickened skim	≥6.5	8.0–10.0
Combustibility (combustion time) after removing burner flame, s:		
six specimens with covers	≤18	5–10
one specimen with cover	≤5	0–3
six specimens without covers	<45	20–25
one specimen without covers	<15	3–8
Oxygen index, %	≥30	35–38
Self-ignition point, °C	>300	450–500

The total time of combustion of six specimens (rings) of commercial TG rubber was 2.0 + 2.2 + 1.8 + 2.0 + 2.2 + 2.0 = 12.2 s (maximal time for single specimen 2.2 s), and that of belt specimens was 2.0 + 3.6 + 4.0 + 4.0 + 4.0 + 3.6 = 21.2 s (maximal time 4.0 s).

According to the vulcanization curve, the induction period of vulcanization is 7 min, and the vulcanization optimum is 30 min; according to the scorching curve, the scorching time is 35 min; the viscosity is 49 Mooney units (Fig. 1).

The presence of four nitrogen atoms and two carbonyl oxygen atoms in the structure of glycoluril as bicyclic bisurea allows it to be considered as fireproofing compound.

Thus, we chose as investigation objects 2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (glycoluril) **1** and its derivatives as heterocyclic fire retardants:



1

Vulcanized rubbers based on synthetic isoprene and divinyl rubbers were used in flame resistance tests.

When performing tests, glycoluril was introduced into the rubber compound in an amount of 5 wt parts (formulation no. 1). The total time of residual combustion of six specimens under consideration was 19.4 s (for separate specimens, 2.8, 3.0, 2.6, 2.6, 5.8, and 2.6 s). The maximal combustion time was 5.8 s (i.e., two times shorter than for the set of six rings of commercial TG grade rubber). From this rubber stock, we prepared six model belt specimens. The specimen size was 300 × 300 mm. The kind of fabric and number of plies were ER-200 × 5. The thickness of external cover layers was 4.5 and 3.5 mm, and the rubber skim thickness was 0.5 mm. Vulcanization was performed under the following conditions: 151°C, 30 min, optimum pressure in pressing rubber compound 140 kgf cm^{-2}. The total time of residual combustion of six model belt specimens was 26.4 s (for separate specimens, 3.8, 4.2, 4.0, 4.0, 7.0, and 3.4 s, maximum 7.0 s). All the physico-mechanical properties of these specimens met the requirements of the regulations (Table 3).

According to vulcanization curve *1* (Fig. 2), the induction period of vulcanization of the mine rubber was 5.5 min, and the vulcanization optimum was 25 min; according to curve *2*, the scorching time was 32.5 min; the viscosity was 49 Mooney units (Table 4).

We suggested a glycoluril derivative, 2,4,6,8-tetramethylol-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (tetramethylolglycoluril) **2** as potential fireproofing agent. Today this compound is mainly used as effective stabilizer for natural and synthetic polymeric products. In addition, the compound is of interest as a monomer for polycondensation.

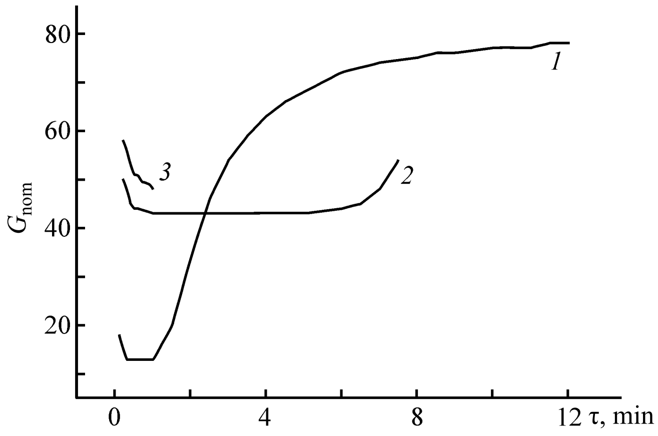


Fig. 1. Kinetic curves of (*1*) vulcanization, (*2*) scorching, and (*3*) viscosity of commercial vulcanized rubber for mines. (G_{nom}) Nominal shear modulus and (τ) time; the same for Figs. 2–6.

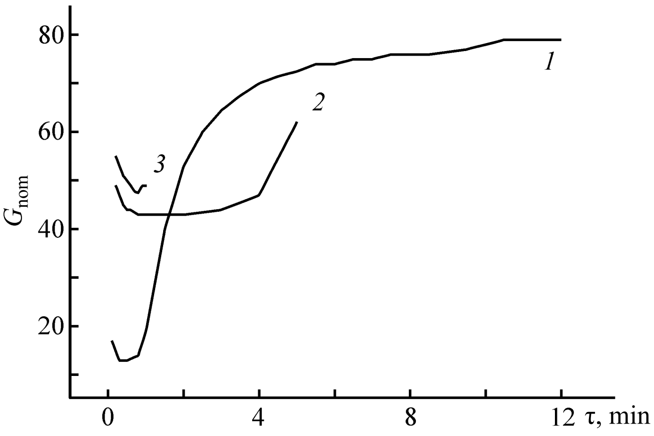
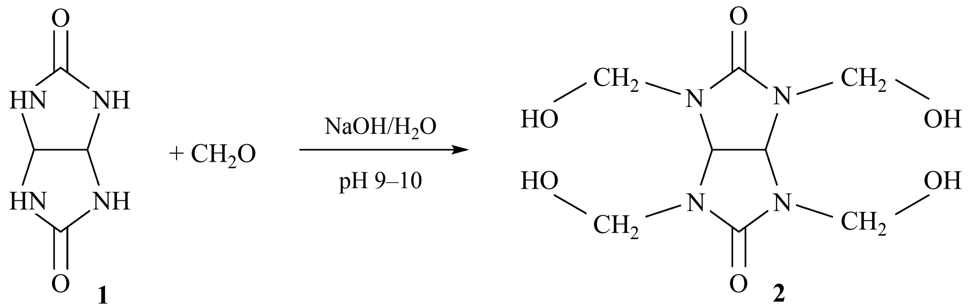


Fig. 2. Kinetic curves of (*1*) vulcanization, (*2*) scorching, and (*3*) viscosity of rubber stock prepared in accordance with formulation no. 1.

The possibility of using **2** as fireproofing additive is determined by the fact that the hydroxy groups present in its structure make it similar to polyols used as fireproofing additives, which are capable to form protective intumescent coatings on the surface of polymer materials:



1 **2**

To perform tests, compound **2** was introduced into the rubber compound in an amount of 10 wt parts (formulation no. 2). The total time of residual combustion of six tested specimens was 9 s (for separate specimens,

Table 3. Physico-mechanical properties of flame-resistant rubbers tested

Formulation	Nominal tensile strength, MPa	Relative elongation at break, %	Abrasion loss, mm^3	Shore hardness A, units	Combustion (rings)
Prescribed level	≥14.7	≥350	≤200	55–70	15–45
TG series	16.3	400	112	72	12.2–2.2
No. 1	14.9	420	102	66	19.4–5.8
No. 2	10.9	570	137	22	9.0–1.6
No. 3	13.7	410	121	68	13.8–3.0
No. 4	15.9	460	107	63	13.2–2.4
No. 5	16.8	440	91	72	11.8–2.4

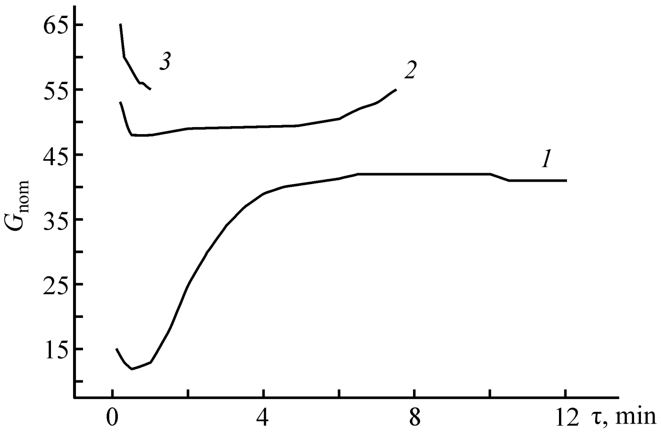
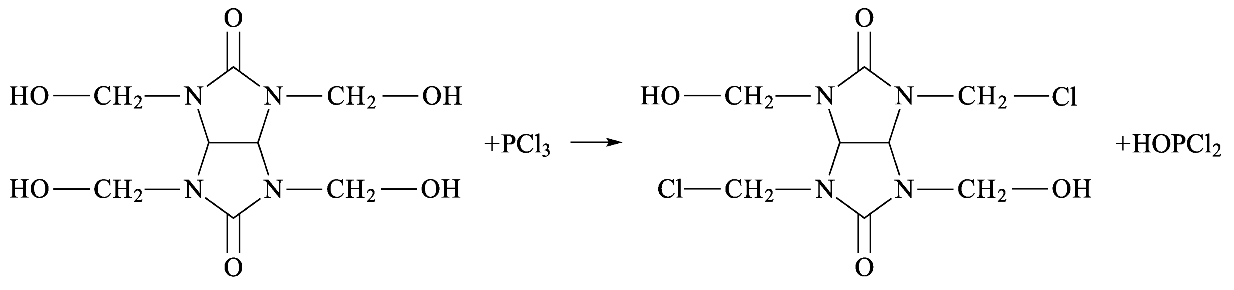


Fig. 3. Kinetic curves of (*1*) vulcanization, (*2*) scorching, and (*3*) viscosity of rubber stock prepared in accordance with formulation no. 2.

1.6, 1.6, 1.2, 1.6, 1.6, and 1.4 s). From this rubber stock, we prepared six model belt specimens. The specimen size was 300 × 300 mm. The kind of fabric and number of plies were ER-200 × 5. The thickness of external cover layers was 4.5 and 3.5 mm, and the rubber skim thickness was 0.5 mm. Vulcanization was performed under the following conditions: 151°C, 35 min, optimum pressure in rubber compound pressing 140 kgf cm^{-2}. The total time of residual combustion of the six model belt specimens was 16.8 s (for separate specimens, 2.8, 2.8, 3.2, 2.4, 3.0, and 2.6 s, maximum 3.2 s). The rubber demonstrated excellent flame resistance, but introduction of **2** negatively affected certain physico-mechanical properties, namely, the nominal tensile strength of the vulcanized rubber specimens was appreciably lower (10.9 MPa) than the level prescribed by the regulations (Table 3).

According to vulcanization curve *1* (Fig. 3), the induction period of vulcanization of the tested rubber was 5.5 min, and the vulcanization optimum was 20.5 min; according to curve *2*, the scorching time was 35 min; the Mooney viscosity was 55 units (Table 4).

Halogenated organic derivatievs are promising fireproofing agents for reducing the combustibility of heat-resistant vulcanized rubbers based on ethylene–propylene rubber. This is due to the fact that halogenated inhibitors operate both in the gas phase and in the gas flame; they inhibit chemical reactions and decrease the flame temperature. Addition of small amounts of halogenated inhibitors decreases the flame propagation velocity by a factor of several tens and influences the ignition limits. 2,6-Di(chloromethyl)-4,8-dihydroxy-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione **3** seems promising in this respect:



2 **3**

When performing tests, compound **3** was introduced into the rubber compound in an amount of 1 wt part (formulation no. 3). The total time of residual combustion of the six tested specimens was 13.8 s (for separate specimens, 2.2, 2.6, 3.0, 2.0, 2.0, and 2.0 s, respectively). The maximal time of combustion of one specimen was 3.0 s, i.e., it was almost two times shorter than the maximal combustion time of the rubber specimen with glycoluril (5.8 s). The nominal tensile strength of these specimens slightly decreased, the scorching time decreased sharply, and the additivity in the fireproofing effect relative to the commercial vulcanized rubber was lacking; nevertheless, all these parameters were within the ranges prescribed by the regulations. However, the results of studying the combustibility and physico-mechanical properties of the rubber compound prepared in accordance with formulation no. 3 showed that performing further tests with belt specimens was inappropriate.

According to vulcanization curve *1* (Fig. 4), the induction period of vulcanization of this rubber was 4 min, and the vulcanization optimum was 24 min; according to curve *2*, the scorching time was 20 min; the viscosity was 48 Mooney units (Table 4).

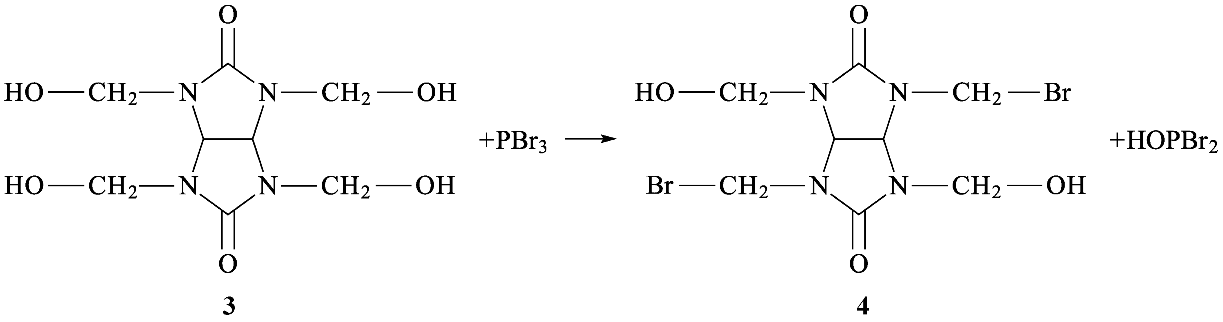
Table 4. Characteristics of vulcanization of the tested rubbers

Formulation	Induction period, min	Optimum, min	Scorching time, min	Viscosity, Mooney units
TG series	7	34	35	50
No. 1	5.5	25	32.5	49
No. 2	5.5	20.5	35	55
No. 3	4	20	22	48
No. 4	4	14	30	46
No. 5	6	28	32	49

The data obtained can be accounted for by the fact that introduction of chlorine leads to changes in the nature and amount of volatile products formed in the course of degradation of polymer materials. The combustibility of polymer materials depends significantly not only on the quantitative content of chlorine, but also on the mechanism of thermal degradation of the polymer material.

A study of fireproofing properties of various halogenated additives has shown that brominated fireproofing agents considerably surpass in performance their chlorinated analogs. This is due to the fact that the brominated fireproofing agents are less volatile than their chlorinated analogs. In addition, brominated fireproofing agents decompose in a narrow temperature interval, ensuring the optimum concentration of bromine in the gas phase, in contrast to their chlorinated analogs, which release chlorine in a wide temperature interval, so that the content of chlorine in the gas phase is low.

Therefore, it was interesting to test 2,6-di(bromomethyl)-4,8-dihydroxy-2,4,6,8-tetraazabicyclo[3.3.0]-octane-3,7-dione **4** as potential fireproofing agent:



3 **4**

To perform the tests, compound **4** was introduced into the rubber compound in an amount of 4 wt parts (formulation no. 4). The total time of residual combustion of the six test specimens was 13.2 s (for separate specimens, 2.0, 2.2, 2.4, 2.0, 2.4, and 2.2 s). The maximal combustion time for a single specimen was 2.4 s and did not differ significantly from that for the rubber compound with compound **3** (3.0 s). However, introduction of **4** led to significant improvement of many mechanical parameters and to appreciable enhancement of the flame resistance relative to formulation no. 3. From this rubber stock, we prepared six belt specimens. The specimen size was 300 × 300 mm. The kind of fabric and number of plies were ER-200 × 5. The thickness of external cover layers was 4.5 and 3.5 mm, and the rubber skim thickness was 0.5 mm. Vulcanization was performed under the following conditions: 151°C, 30 min, optimum pressure in rubber compound pressing 140 kgf cm^{-2}. The total time of residual combustion of the six model belt specimens was 19.0 s (for separate specimens, 3.4, 2.8, 3.0, 3.0, 2.8, and 4.0 s, maximum 4.0 s).

According to vulcanization curve *1* (Fig. 5), the induction period of vulcanization of the tested rubber

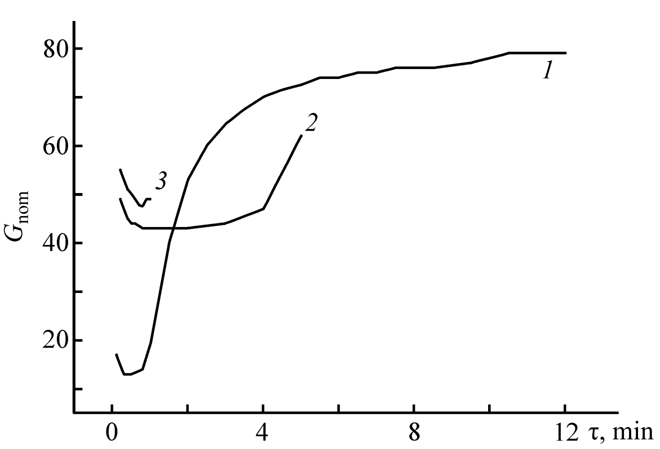


Fig. 4. Kinetic curves of (*1*) vulcanization, (*2*) scorching, and (*3*) viscosity of rubber compound prepared in accordance with formulation no. 3.

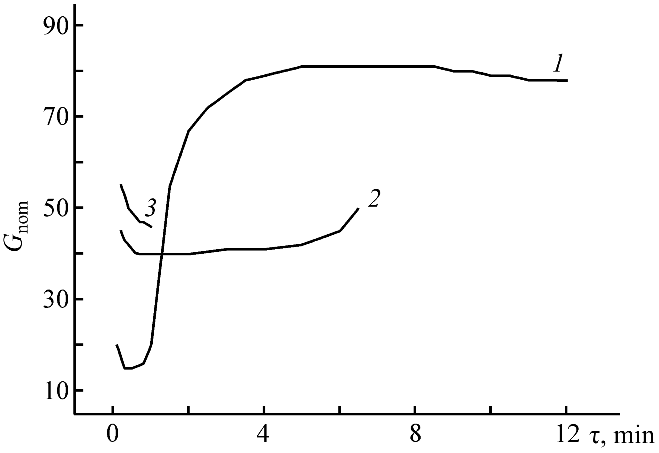
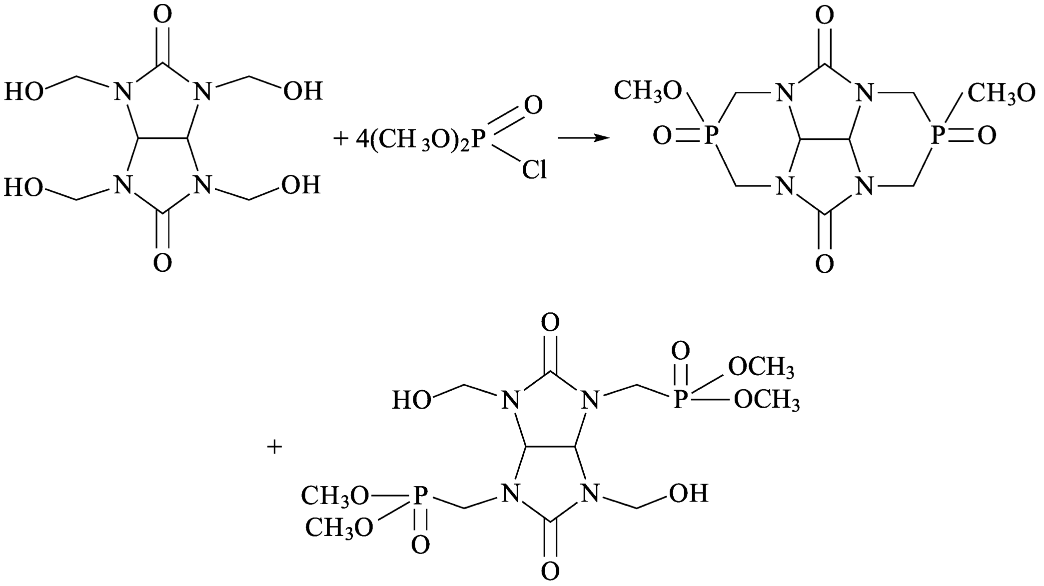


Fig. 5. Kinetic curves of (*1*) vulcanization, (*2*) scorching, and (*3*) viscosity of rubber compound prepared in accordance with formulation no. 4.

was 4 min, and the vulcanization optimum was 14 min; according to curve *2*, the scorching time was 30 min; the Mooney viscosity was 46 units (Table 4). These values show that the vulcanization characteristics of this rubber are quite acceptable.

Search for new organophosphorus fireproofing agents, which are environmentally safer and more effective fire retardants, is actively performed in the world. They can also catalyze coking on the material surface, thus enhancing the fire protection.

The presence of nitrogen-containing fragments in phosphorus-containing polymers facilitates the formation of polyphosphoric acid, which is a dehydrating and phosphorylating agent and a coking catalyst. Also, nitrogen- and phosphorus-containing mixtures or compounds formed in the course of their degradation are substances decomposing with the release of water and carbon; the release of combustion-inhibiting volatile nitrogen compounds and the formation of protective heat-resistant coatings of phosphorus and nitrogen compounds on the material surface are also possible:



To perform tests, a mixture of polyfunctional products **5** and **6** was introduced into the rubber compound in an amount of 0.8 wt part (formulation no. 5). The total time of residual combustion of the six tested specimens was

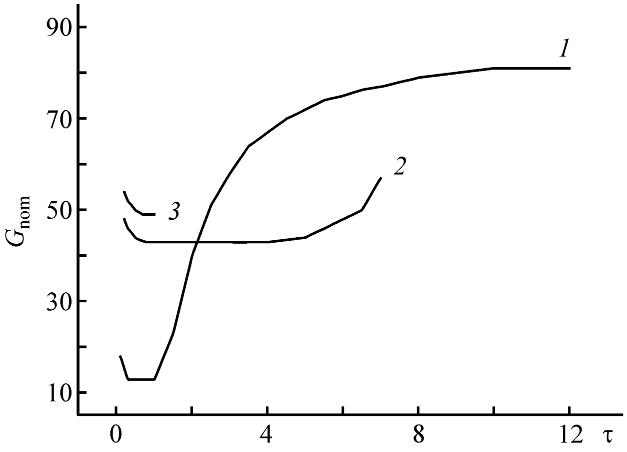


Fig. 6. Kinetic curves of (*1*) vulcanization, (*2*) scorching, and (*3*) viscosity of rubber stock prepared in accordance with formulation no. 5.

11.8 s (for separate specimens, 1.4, 2.0, 2.0, 1.8, 2.2, and 2.4 s). The maximal combustion time of single specimen was 2.4 s, being close to that of the rubber specimen with **3** (3.0 s). From this rubber stock, we prepared six belt specimens. The specimen size was 300 × 300 mm. The kind of fabric and number of plies were ER-200 × 5. The thickness of external cover layers was 4.5 and 3.5 mm, and the rubber skim thickness was 0.5 mm. Vulcanization was performed under the following conditions: 151°C, 30 min, optimum pressure in rubber stock pressing 140 kgf cm^{-2}. The total time of residual combustion of the six model belt specimens was 19.8 s (for separate specimens, 3.0, 3.6, 4.6, 2.4, 2.4, and 3.8 s, maximum 4.6 s). Even on adding so small amounts of **5** + **6**, the rubber vulcanization rate increased, and the scorching time slightly decreased compared to the commercial TG rubber.

According to vulcanization curve *1* (Fig. 6), the induction period of vulcanization of the tested rubber was 6 min, and the vulcanization optimum was 28 min; according to curve *2*, the scorching time was 32 min; the viscosity was 49 Mooney units (Table 4).

On the whole, the tested rubbers with the addition of bicyclic bisurea derivatives demonstrated satisfactory levels of flame resistance and physico-mechanical parameters. The rubbers with the addition of tetra-*N*-methylolglycoluril **2**, 2,6-di(bromomethyl)-4,8-dihydroxy-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-doine **4**, and polyfunctional compounds **5** and **6** exhibit the best flame resistance among the tested samples of vulcanized rubber based on synthetic isoprene and divinyl rubbers.

However, as far as physico-mechanical properties are concerned, the rubbers with the addition of bromine- and phosphorus-containing derivatives showed the best results. All the tests were performed on the base of the Research Center for Polymer Materials at the Eurasian Industrial Chemical Group (Karaganda) and were documented.

CONCLUSIONS

(1) Convenient procedures were developed for preparing new bicyclic bisurea derivatives (glycolurils) functionalized with halo- and dimethoxyphosphorylmethyl groups via tetra-*N*-methyloglycoluril. The compounds synthesized exhibit high performance as fireproofing additives to vulcanized rubbers based on synthetic isoprene and divinyl rubbers.

(2) Five rubber formulations containing the suggested fireproofing compounds were considered using TG grade (difficultly combustible) mine rubber as reference standard. The vulcanized rubber with the addition of tetra-*N*-methylolglycoluril and of halomethyl and phosphorylmethyl glycoluril derivatives exhibits the highest flame resistance among the tested samples of vulcanized rubbers based on synthetic isoprene and divinyl rubbers.

(3) Even small additions of bromine- and phosphorus-containing glycoluril derivatives as fireproofing agents increase the rubber vulcanization rate and slightly decrease the scorching time relative to the initial rubber of TG grade.

REFERENCES

1. Kodolov, V.I., *Zamedliteli goreniya polimernykh materialov* (Fire Retardants for Polymeric Materials), Moscow: Khimiya, 1980.
2. Korshak, V.V., *Termostoikie polimery* (Heat-Resistant Polymers), Moscow: Khimiya, 1989.
3. Zaikov, G.E. and Lomakin, S.M., *Ecological Aspects of Polymer Flame Retardancy*, Brill Academic, 1999.
4. RF Patent 2344140, Publ. 2009.
5. Shmakov, A.G., Korobeinichev, O.P., Shvartsberg, V.M., et al., *Fiz. Goren. Vzryva*, 2006, vol. 42, no. 6, pp. 64–73.