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## Regarding the Reaction of Polysulphides of 2-*tert*-Butylphenol with Rubber and Heptene-1 in Inert Atmosphere and in Air

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### Abstract

Heating heptene-1 in the presence of di- and polysulphides of 2-*tert*-butylphenol (stabilizer thioalcofen B, TAB), yields isomeric S-heptyl thiophenol derivatives at 200 °C in an inert atmosphere in good yields. When this reaction is carried out in the air, heptene-1 dimerization and trimerization products are formed. Like initial heptene, they are oxidized with atmospheric oxygen to yield aliphatic alcohols and esters. This observation of the grafting of sulphur-containing fragments to the alkene formed the basis for experiments with an olefin polymer, rubber. The thermal processing of butadiene-nitrile rubber compounds in the presence of 2-*tert*-butylphenol-based sulphur-containing compounds results in thermolysis of polysulphide components of stabilizer TAB to form 4-mercaptophenol derivatives and rubber-unextractable thermolysis products, which testifies their grafting. The technical performance of rubber-containing fragments of compounds being part of stabilizer TAB was acquired. An opportunity to use this rubber with the grafted antioxidant for the manufacture of products that are in contact with solvents was demonstrated.

**Keywords:** di- and polysulphides of 2-*tert*-butylphenol, thermolysis, reactions of olefins, graft polymers, grafting of antioxidants, derived rubber, its properties

### INTRODUCTION

In recent decades, there is an increasing interest towards the exploration of olefin reactions, including polymer species. This is driven by an opportunity for the chemical grafting of functional groups thereto, which results in a surprising change in properties. This particularly appears for polymers alkenes that yield polymeric materials with exceptional resistance towards environmental exposure via chemical transformations. Making such materials is relevant for Rus-

sia, as it ensures the sustainable development of its economy under adverse climatic conditions.

The development of territories in the northern climatic zone of Yakutia requires making and using machines that contain polymer products in a special performance of their strength and durability. Among relevant tasks, improving the mechanical and other properties of rubbers and rubber products is of importance.

A new area of synthesis and production of durable graft-polymers with various properties has begun evolving rapidly in polymer chemistry. It

is known that thermo- and light stabilizers grafted to polymeric materials make it possible to produce products therefrom that operate under extreme operating conditions: at high and low temperatures, in vacuum, in contact with water, solvents, and aggressive media [1].

Synthesis of graft-polymers is based on reactions with low-molecular-mass olefins under solvent- and waste-free conditions, which meets the requirements imposed on large-tonnage polymer production and fundamental principles of sustainable development.

In our view, the area of polymer modification, where not active chemicals but their low-volatile precursors, such as di- and polysulphides of sterically hindered phenols, are used, is promising. The thermal processing of polymer compounds together with the indicated species leads to their thermolysis to form mercaptans and also phenoxy and other particles that are added to the double bond of olefins, each in its own mechanism [2]. Synthesis of high-impact polystyrene using 2,6-di-*tert*-butyl-4-(3-mercaptopropyl)phenol that is a source of the polymer skeleton-grafted mercaptan containing a fragment of the sterically hindered phenol in its structure, ensuring stability and high quality of the polymer material, may be considered as a successful approach to the synthesis of graft polymers [3]. To the present time, there are known successful practical examples of the use of phenol di- and trisulphides to stabilize and notably improve mechanical properties of polymer compounds made of sevilen [4], glass fibre reinforced polyamide [5], and fibreglass [6].

Two latest research works used stabilizer thioalcofen B (TAB) as a mercaptan precursor. When it is synthesized from 2-*tert*-butylphenol and disulphur dichloride, a mixture of sulphur-containing compounds, such as mono-, di-, and polysulphides, is generated [7]. The main components of the resulting mixture are 4,4'-thiobis(2-(*tert*-butyl)phenol) **1** (12 %), 4,4'-disulphanediylbis(2-(*tert*-butyl)phenol) **2** (30 %), 4,4'-trisulphanediylbis(2-(*tert*-butyl)phenol) **3** (24 %), and 4,4'-tetrasulphanediylbis(2-(*tert*-butyl)phenol) **4** (11 %); the rest is 2-*tert*-butylphenol *o,p*-mono- and *o,p*-polysulphides (in total, 6 %), and also three 2-*tert*-butylphenol-containing fragments (11–12 %).

The use of the stabilizer TAB as a source of compounds grafted to molecules of polymers during their thermal treatment to form graft polymers allows modifying polymer compounds. Reference [8] reports on the use of graft polymers to be grafted to metal conductors by the formation of

sulphide bridge between the surfaces of the coating and the metal stable at temperatures as high as 110 °C. There is a similar phenomenon when using modifier TAB during generating a coating for epoxy resins-based metal conductors [9]. Components generated by thermolysis are chemically bound with epoxy resin, whereupon there is an opportunity to form bonds of the coating and its high adhesion to a metal surface.

Data was acquired earlier on modification of rubber by grafting a phenolic antioxidant based on phenolic di- and trisulphides thereto. Nevertheless, it is worth paying attention to an indication of paper [10] testifying a negative effect of antioxidants containing longer chains of sulphur atoms on the mechanical properties of polymers. Apparently, there should be harmonically reducing action of antioxidants with oxidative properties of sulphur in the structure of these products.

The authors of [10] also demonstrated that the joint presence of antioxidant of a group of aromatic amines and antioxidant additive (naphtham-2 or alnaft) increased the resistance of rubbers to ageing and products operability by 1.5 times.

The stabilizer TAB contains components of different mechanisms of action operating as additives (monosulphide **1**), and also oligosulphides **2–4** able to be grafted to polymer molecules. When exploring the joint action of TAB with additives of aromatic antioxidants, it was concluded of good antioxidant properties of rubbers containing this mixture. A useful property of antioxidant TAB is the ability to slightly change the mechanical properties of polymer compounds [11]. It was also shown in this work that stabilizer TAB containing 50 % of di- and polysulphides demonstrated good antioxidant properties.

Varying preparation conditions for stabilizer TAB during its synthesis, one may change the ratio of additives and grafted components. An increase in the content of the latter was reached by the use of *N,N*-dimethylformamide as a solvent: the amount of monosulphides was reduced to 16 % with increasing the amount of di- (34 %), tri- (28 %), and tetrasulphides (17 %) [7], which turned out to be expedient in achieving rubber performance.

As determined in paper [12] on examining the effect of stabilizing components of TAB on properties of the resulting rubbers, it is a vulcanization accelerator. This effect is enhanced by 1.2 times during its joint use with an industrial vulcanization accelerator that is thiuram D (tetramethyl thiuram disulphide).

The purpose of this research was to explore the effect of stabilizer TAB with an enriched content of di- and polysulphide components on rubber properties, and also to determine the chemism of the grafting of TAB thermolysis products to polymers.

## RESULTS AND DISCUSSION

The work used butadiene-nitrile rubber SKN-26 ASM purified from stabilizing additives contained therein by their long extraction with boiling ethanol from the rubber. The introduction of antioxidants into the purified rubber was carried out on rollers heated to the required temperature (processing step).

The efficiency of antioxidants was assessed by comparison of results for initial properties of rubber samples with those for stabilized specimens obtained in the processing step and aged in an oven during thermo-oxidative exposure at 100 °C for 120 h (Table 1). As can be seen from the data of physicomechanical investigations on rubber samples, TAB, being an effective modifier, is noticeably superior to industrially used *p*-nitrosophenol according to the specified effect. Moreover, it is more effective than traditional phenolic antioxidants, such as 2,4,6-tri-*tert*-butylphenol (P-23),

monosulphide **1** and N-phenyl- $\beta$ -naphthylamine (naphtham-2) used in industry for the production of rubber products, by the antioxidant effect.

In this manner, modifier TAB exerts a positive combined effect on them, judging by the relatively large retention of their strength and expansion indicators during ageing compared to the above antioxidants and additives. In order to determine the effect of stabilizers TAB not extracted from the polymer, a portion of prepared rubber samples was extracted with acetone for 48 h before their ageing process. Afterwards, mechanical properties of extracted rubber samples were determined after ageing of the latter at 100 °C for 120 h (see Table 1). There was worsening physical properties of the extracted samples in all cases, however, as it follows from the findings, they were reduced by 7 % in rubber samples, which was not so dramatic compared to indicators for rubber specimens containing other antioxidants (property worsening by 50 % and above). In this fashion, the lack of extraction of the bulk of components in an antioxidant made of rubber points to the grafting of ingredients of stabilizer TAB (di- and polysulphides) during thermal processing. In other words, the conclusion about the lack of antioxidant extraction because of their chemical interaction with the polymer compound may be made in a similar way to [13]. A proxy

TABLE 1

Efficiency of phenolic antioxidants in rubber SKN-26 ASM introduced at the mixing step after their ageing at 100 °C for 120 h (the error of changes is not more than  $\pm 5$  %)

Parameters	Stabilizers*			
	P-23 (1.25)	<i>p</i> -Nitrosophenol (0.65)	TAB (2.0)	Monosulphide <b>1</b> (2.0)
<b>Initial sample</b>				
Vulcanization parameters:				
optimum temperature, °C	143	143	143	143
time, min	100	40	100	40
Tensile modulus, MPa	86	76	56	52
Tensile strength, MPa	26.87	30.01	26.38	30.13
Elongation, %	630	590	690	750
<b>Aged sample</b>				
<i>Unexposed to extraction</i>				
$K_{\sigma}$	0.45	0.56	0.87	0.67
$K_L$	0.21	0.22	0.49	0.26
<i>After extraction with acetone</i>				
$K_{\sigma}$	0.34	0.47	0.81	0.60
$K_L$	0.07	0.20	0.3	0.28

Note.  $K_{\sigma}$  and  $K_L$  are changes in relative tensile strength and relative elongation after ageing (in fractions of initial values). TAB is thioalcofen B.

\* Stabilizer content (ppm) in compound is given in brackets.

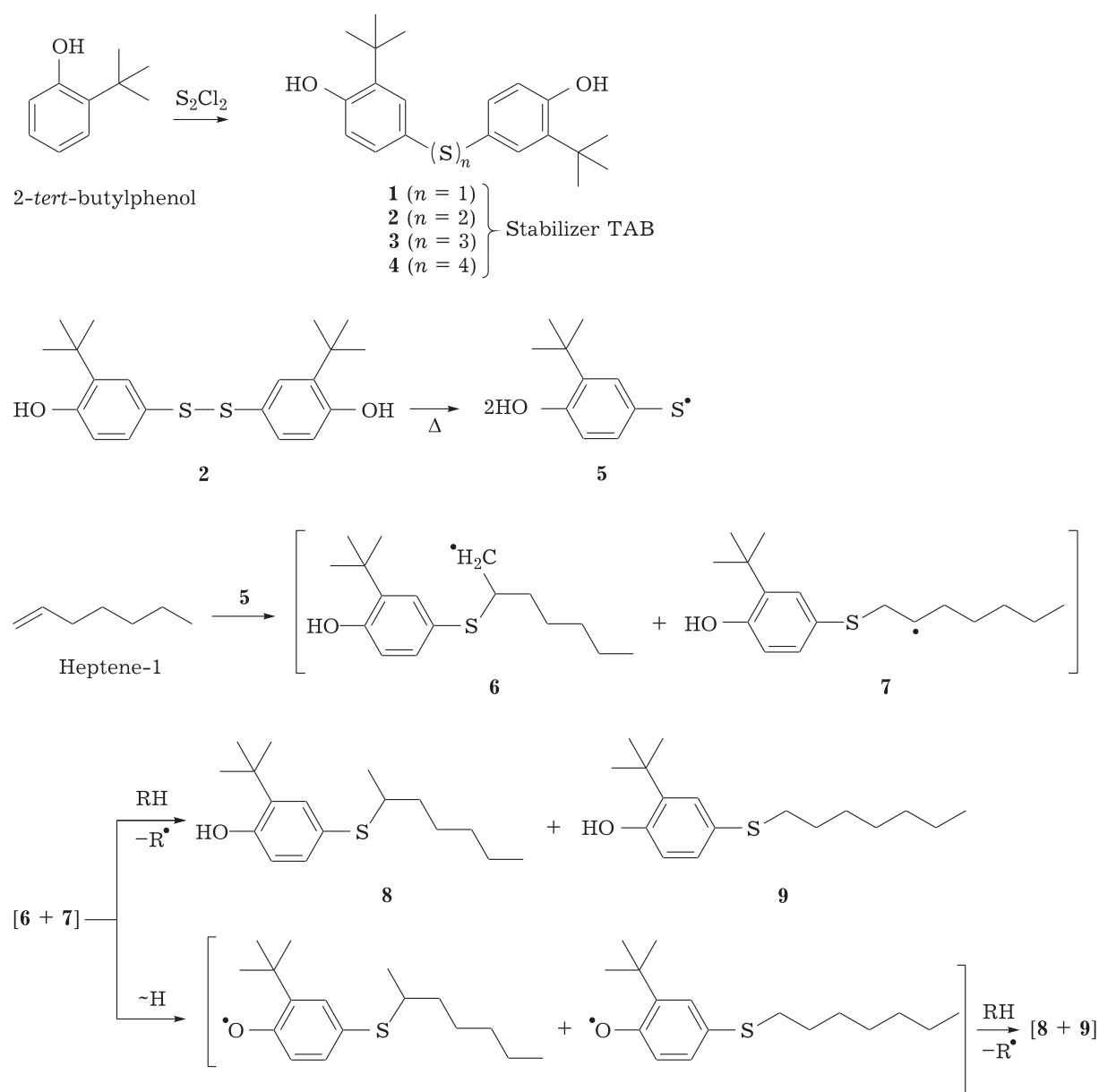
indicator of grafting polymer chains of rubber toward one another in the presence of TAB is a reduced tensile modulus.

In order to investigate processes proceeding during joint thermal treatment of rubber and components of thioalcofen B, a model reaction of TAB with heptene-1 was carried out in the inert atmosphere and in air at 200 °C.

The suggested interaction path of components of TAB with heptene-1 on an example of thermal transformations of the main component of TAB that is disulphide **2** is given Scheme 1. According to it, radical **5** formed during thermolysis of compound **2** at the S-S bond is added to the hep-

tene-1 molecule, which results in the formation of isomeric radicals **6** and **7** that are further reduced under the influence of antioxidants (or hydrocarbons) giving the final products, isomeric heptylphenol compounds **8** and **9**. The latter species were isolated using column chromatography as a mixture in a 7 : 1 mole ratio of isomers.

Furthermore, 7 % of monosulphide **1**, 5 % of 2-*tert*-butylphenol, and 3 % of diheptyl sulphide compounds alongside with isomeric sulphides **8** and **9** in a 7 : 1 ratio (in total, 85 %) were recorded in reaction products of antioxidant TAB and heptene-1 using GS-MS. Judging by the composition of the products formed, as in [2], a minor

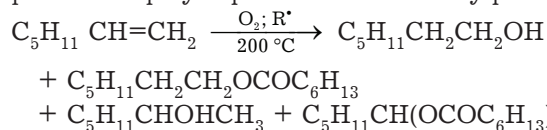


Scheme 1.

process related to the rupture of the Ar-S bond in disulphide **2** is also possible, leading to 2-*tert*-butyl phenol and the formation of sulphur that yields diheptyl sulphide compounds in the reaction with heptene-1.

When heptene-1 reacts with stabilizer TAB in air at 200 °C, apart from the main process of addition of sulphide radical **5** to the C=C double bond of heptene-1 leading to the formation of compounds **8** and **9**, there are paths of transformation of heptene-1. It was determined that the main products of the transformation of heptene-1 in the presence of air oxygen were its dimerization and trimerization products (tetradecene compounds, pentadecylcyclohexane, and acylcyclohexane derivatives isomeric to it), and also oxidation products of these olefins: aliphatic alcohols and esters, the process of formation of which required more detailed consideration.

Initially, it may be assumed that the formation of dimeric olefins, oxidation of heptene and these olefins by air oxygen according to Scheme 2 is catalysed by radicals formed during thermal decomposition of polysulphides of 2-*tert*-butylphenol:



Oxidation of olefins to alcohols with air oxygen proceeding under the influence of phenoxy radicals formed from phenolic antioxidants present in the system (their oxidation catalyst is gold on the substrate) may be viewed as an analogue of these processes [14].

Another important and practically significant evidence of the efficiency of TAB as an antioxidant is the lack (according to GC-MS) of oxidation products of compounds **1-4**, **8**, and **9**, and also diheptyl sulphide species at the sulphur atom: sulphones, sulphoxides, and products of oxidative cleavage of the C-S bond. Based on this one may suggest resistance of components of TAB towards air oxygen oxidation at the sulphur atom during thermal processing with rubbers followed by products operation at elevated temperatures in the air [15]. Thus, TAB components are not only grafted to polymer molecules, which prevents their washing-out, but are also able to be preserved in the polymeric mass during heating in the presence of air oxygen, which hinders their removal for the reason of oxidative decomposition including when contacting solvents.

The structure of compounds **8** and **9** was proven by <sup>1</sup>H and <sup>13</sup>C NMR, and also by high resolution

MS. The <sup>1</sup>H NMR spectrum of these species contains the signals expected for hydrogen atoms of aromatic fragments (6.59 d (H<sup>6</sup>), 7.14 dd (H<sup>5</sup>), 7.34 d (H<sup>3</sup>) for compound **8** and 6.59 d (H<sup>6</sup>), 7.10 dd (H<sup>5</sup>), and 7.30 d (H<sup>3</sup>) for its isomer **9**). A multiplicity of signals of the aromatic moiety in species **8** and **9** unambiguously corresponds to multiplicities of signals of 1,2,4-benzene compounds. Differences in the structure of alkyl substituents result in the difference in chemical shifts values for H<sup>3</sup> and H<sup>5</sup> in spectra of compounds **8** and **9**, which is quite expected due to a close location of the alkylthio group to the indicated hydrogen atoms but almost do not have impact on chemical shifts values for the H<sup>6</sup> signal located away from the alkylthio group.

The spectrum of these compounds also have the following signals of aliphatic substituents: singlets of *tert*-butyl hydrogen atoms (1.37 ppm for **8** and 1.39 ppm for **9**), a triplet of the methyl group of *n*-pentyl (**8**) or *n*-hexyl (**9**) substituents (0.86 ppm, characteristic signals of the aliphatic substituent of compound **8**, a doublet (1.20 ppm) of hydrogen atoms of the methyl group (SCHCH<sub>3</sub>) and the signal of the hydrogen atom of the methine moiety (SCHCH<sub>3</sub>) as a quadruplet of triplets (2.98 ppm), as well as intrinsic signals of the aliphatic fragment of compound **9**, a signal of hydrogen atoms of the methylene fragment (SCH<sub>2</sub>) as a triplet (2.79 m). The fact that the <sup>1</sup>H NMR spectra of compounds **8** and **9** were recorded for their mixture explains the difficulty of detailed analysis of signals of hydrogen atoms in aliphatic substituents (determination of multiplicity, the precise assignment, and the position of signals for diastereotopic atoms).

Their <sup>13</sup>C NMR spectrum contains the signals expected for carbon atoms of the aromatic fragment [116.80 (C<sup>6</sup>), 136.46 (C<sup>2</sup>), 153.93 (C<sup>1</sup>), 116.97 (C<sup>6</sup>), 136.67 (C<sup>2</sup>), and 153.28 (C<sup>1</sup>) for compounds **8** and **9**, respectively] and aliphatic substituents [13.96 (CH<sub>2</sub>CH<sub>3</sub>), 29.35 (C(CH<sub>3</sub>)<sub>3</sub>), 34.45 (C(CH<sub>3</sub>)<sub>3</sub>), and 44.46 (SCH), for **8**, 13.97 (CH<sub>2</sub>CH<sub>3</sub>), 29.33 (C(CH<sub>3</sub>)<sub>3</sub>), and 34.51 (C(CH<sub>3</sub>)<sub>3</sub>) for **9**, correspondingly].

## CONCLUSION

Resulting from the research undertaken, it has been demonstrated that stabilizer thioalcofen B (TAB) containing as high as 80 % of di- and polysulphides, is of a complex action, non-staining polymers with the polyfunctional product and may be of significant interest for manufacturing rubbers that are in contact with solvents, as it ensures



a sufficient degree of permanence of their properties. This was found on the basis of comparison of mechanical and antioxidant properties of acetone-extracted and unextracted rubber samples after their thermal ageing.

Transformations picture of thermolysis products of antioxidant TAB components during their grafting to the substrate has been revealed. Reaction products of TAB and heptene-1 modelling the chemical behaviour of rubber in an inert atmosphere and in air have been determined. The interaction of heptene-1 and its dimerization and trimerization products with air oxygen resulting in the formation of the corresponding alcohols and ethers from olefins has been detected. It has been demonstrated that thioalcofen B shows high antioxidant activity, significantly slowing down the oxidation process of heptene-1 and preventing oxidation of alkylaryl and dialkyl sulphides that are interaction products of components of TAB with the alkene. Thus, it is worth assuming that components of fragments of TAB formed resulting from their grafting to polymer substrate are able to tolerate air oxygen exposure at a high temperature without the removal from rubber as a result of oxidation decomposition.

## EXPERIMENTAL

The composition of a mixture of reaction products of heptene-1 and TAB was determined using the Agilent 6890N gas chromatograph under the following conditions: 1) sample volume of 0.2  $\mu\text{L}$ ; 2) the HP-5MS chromatographic column (30 m  $\times$  0.25 m  $\times$  0.25  $\mu\text{m}$ ); 3) the split ratio method of recording (SPLIT), 150 : 1; 4) injector temperature of 300  $^{\circ}\text{C}$ , heating conditions of 2 min at 50  $^{\circ}\text{C}$  followed by ageing at 300  $^{\circ}\text{C}$  for 20 min. The total analysis time was 84.5 min.

The  $^1\text{H}$  ЯMP and  $^{13}\text{C}$  NMR spectra were recorded using Bruker AV-400 and Bruker DRX-500 spectrometers (operating frequency were 400.13 MHz for  $^1\text{H}$  and 125.76 MHz for  $^{13}\text{C}$ , respectively) for solutions in  $\text{CDCl}_3$ . The NMR  $^1\text{H}$  и  $^{13}\text{C}$  chemical shifts were measured against solvent residual signals in  $\text{CHCl}_3$  ( $\delta_{\text{H}}$  7.24 ppm and  $\delta_{\text{C}}$  76.90 ppm).

Column chromatography was performed using Alfa Aesar silica gel (60–200 nm) with petroleum ether 0–70  $^{\circ}\text{C}$  (Ecos-1); the solvent was distilled over  $\text{P}_2\text{O}_5$  and ethyl acetate (the solvent was dried over  $\text{NaHCO}_3$  and  $\text{CaCl}_2$ , and then distilled over  $\text{P}_2\text{O}_5$ ).

Samples of TAB with contents of di- and trisulphides of not less than 80 % were produced under standard conditions in the Pilot Chemical Production of N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry. The experiments used a sample of heptene-1 with a content of 99 mass %. The research work utilised samples of domestically produced antioxidants: P-23 (2,4,6-tri-*tert*-butylphenol), naphtham-2 (N-phenyl- $\beta$ -naphthylamine), and modifier *p*-nitrosophenol.

Experiments for determination of the efficiency of antioxidants for rubber CKN-26 ACM were carried out using the equipment of the Department of Chemistry and Technology of Processing Elastomers of the Siberian State Technological University (Krasnoyarsk). Rubber was pre-purified from antioxidants contained therein by ethanol extraction. The introduction of components in equimolar amounts into the purified rubber was carried out on rolls and subsequent vulcanization – using electropress at a temperature of (142 $\pm$ 2)  $^{\circ}\text{C}$ . Mechanical properties of rubber samples were determined according to GOST 9.024-74 [16] after holding in thermo cabinets for 120 hrs at a temperature of (100 $\pm$ 2)  $^{\circ}\text{C}$ . The efficiency of antioxidants was assessed by comparison of properties of initial rubber compounds with the recorded changes in them after thermal-oxidative exposure. A portion of the prepared rubber samples was extracted with acetone for 48 h before the ageing process. Afterwards, their physical parameters were determined according to GOST 9.024-74 after ageing extracted samples at a temperature of (100 $\pm$ 2)  $^{\circ}\text{C}$  for 120 h.

**Interaction of TAB components with heptene-1 in nitrogen medium.** A solution of 1.0 g of TAB containing 80 % of di- and trisulphides in 10 mL of heptene-1 is placed in a steel rotating autoclave with a capacity of 50 mL. The air inside the autoclave is displaced with nitrogen and the contents are heated during autoclave rotation for 4 hrs at 200  $^{\circ}\text{C}$ . After cooling the autoclave to room temperature, its contents are unloaded. The resulting solution is analysed using the Agilent 6890 N gas chromatograph. According to GC data, not considering the solvent, the reaction mass contained 77 % of a mixture of compound **6** and its isomer **7**, 3 % of diheptyl sulphide compounds, 5 % of *tert*-butylphenol, 8 % of 4,4'-thiobis(2-*tert*-butylphenol), 1 % of mercapto-2-*tert*-butylphenol, and minor amounts of some other compounds.

A mixture of isomeric compounds **8** and **9** was isolated using  $\text{SiO}_2$  column chromatography using petroleum ether and ethyl acetate mixture in a

ratio of 100 : 0 ... 100 : 1 as eluent. A mixture of products **8** and **9** (a 7: 1 molar ratio, according to  $^1\text{H}$  NMR) was obtained in the amount of 0.2 g as a slightly coloured oily liquid with a spicy smell.

**2-(tert-Butyl)-4-(heptane-2-ylthio)phenyl, 8.**

The  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm (J, Hz): 0.86 t (3H,  $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_4\text{CH}_3$ , 7.0 Hz), 1.16–1.46 m (8H,  $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_4\text{CH}_3$ ), 1.20 d (3H,  $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_4\text{CH}_3$ ), 6.7 Hz), 1.37 s (1H,  $\text{C}(\text{CH}_3)_3$ ), 2.98 qt (1H,  $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_4\text{CH}_3$ , 6.7 Hz, 6.5 Hz), 4.90 br s (1H, OH), 6.59 d (1H,  $\text{H}^6$ , 8.1 Hz), 7.14 dd (1H,  $\text{H}^5$ , 8.1 Hz, 2.2 Hz), 7.34 d (1H,  $\text{H}^3$ , 2.2 Hz).

The  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 13.96 ( $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_4\text{CH}_3$ ), 21.00 ( $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_4\text{CH}_3$ ), 22.46 ( $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_3\text{CH}_2\text{CH}_3$ ), 26.58 ( $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ ), 29.35 ( $\text{C}(\text{CH}_3)_3$ ), 31.59 ( $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 34.45 ( $\text{C}(\text{CH}_3)_3$ ), 36.35 ( $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_3\text{CH}_3$ ), 44.46 ( $\text{SC}(\text{CH}_3)\text{H}(\text{CH}_2)_4\text{CH}_3$ ), 116.80 ( $\text{C}^6$ ), 124.62 ( $\text{C}^4$ ), 132.78, 133.37 ( $\text{C}^3$  and  $\text{C}^5$ ), 136.46 ( $\text{C}^2$ ), 153.93 ( $\text{C}^1$ ).

High resolution mass spectrometry: found  $m/z$  280.1856 [ $M$ ] $^+$ ,  $\text{C}_{17}\text{H}_{28}\text{O}_1\text{S}_1$ , calculated  $M$  280.1855. The mass spectrum,  $m/z$ , %: 280 ( $M^+$ , 80), 183 (12), 182 (100), 169 (13), 167 (74), 150 (13), 139 (14), 135 (30), 107 (21), 57 (20), 41 (14).

**2-(tert-Butyl)-4-(heptylthio)phenol, 9.**

The  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm (J, Hz): 0.86 t (3H,  $\text{SCH}_2(\text{CH}_2)_5\text{CH}_3$ , 7.0 Hz), 1.16–1.46 m (6H,  $\text{SCH}_2(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$ ), 1.39 s (1H,  $\text{C}(\text{CH}_3)_3$ ), 1.48–1.60 m (4H,  $\text{SCH}_2(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$ ), 2.79 t (2H,  $\text{SCH}_2(\text{CH}_2)_5\text{CH}_3$ , 7.4 Hz), 4.85 br s (1H, OH), 6.59 d (1H,  $\text{H}^6$ , 8.1 Hz), 7.10 dd (1H,  $\text{H}^5$ , 8.1 Hz, 2.2 Hz), 7.30 d (1H,  $\text{H}^3$ , 2.2 Hz).

The  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 13.97 ( $\text{SCH}_2(\text{CH}_2)_5\text{CH}_3$ ), 22.48 ( $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{CH}_3$ ), 28.56, 28.74, 29.24 ( $\text{SCH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{CH}_3$ ), 29.33 ( $\text{C}(\text{CH}_3)_3$ ), 31.44 ( $\text{SCH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{CH}_3$ ), 34.51 ( $\text{C}(\text{CH}_3)_3$ ), 35.76 ( $\text{SCH}_2(\text{CH}_2)_5\text{CH}_3$ ), 116.97 ( $\text{C}^6$ ), 126.41 ( $\text{C}^4$ ), 129.97, 130.69 ( $\text{C}^3$  and  $\text{C}^5$ ), 136.67 ( $\text{C}^2$ ), 153.28 ( $\text{C}^1$ ).

The mass spectrum,  $m/z$ , %: 280 ( $M^+$ , 100), 265 (26), 182 (20), 167 (46), 139 (23), 115 (13), 57 (44), 55 (44), 43 (37), 41 (45).

**Interaction of components of TAB with heptene-1 in air.** A solution of 1.0 g TAB in 10 mL of heptene-1 is placed in a steel rotating autoclave with a capacity of 50 mL. The autoclave is closed and heated with rotation to 200 °C ageing for 4 h. Products are extracted after cooling the autoclave and the resulting mixture is analysed using the Agilent 6890 N gas chromatograph-mass spectrometer (GC-MS).

The mixture contains compounds **8** and **9** in the amount of 28 %, diheptyl sulphide compounds (3 %), 2-tert-butylphenol (7 %), alkenes (three iso-

mers of tetradecene – in total, 4.7 %, pentadecene – 0.5 %), totally 5.2 %, aliphatic alcohols (1-hexene-3-ol – 9.4 %, 2-hepten-1-ol – 3.7 %, 1,2-octanediol – 0.4 %, 4,8-dimethylnonanol – 0.4 %, 1,15-pentadecanediol – 3.1 %), in total, 19 %, carboxylic acids esters (0.4 % hexanoic acid butenyl ester, carboxylic acids esters:  $M = 244$  g/mol – 0.75 %,  $M = 184$  g/mol – 2.0 %,  $M = 214$  g/mol – 0.2 %),  $M = 294$  g/mol – 0.3 %, in the amount of 3.7 %.

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## REFERENCES

- Gurvich Ya. A., Kumok S. T., Lopatin V. V., Starikova O. F., Phenolic Antioxidants. Current State and Prospects, Moscow: TSNIITeneftkhem Publishing Office, 1990, Issue 5. P. 76. ISSN 0205-700X. (in Rus.).
- Krysin A. P., Pokrovskij L. M., Nefedov A. A., Shundrina I. K., Selivanov B. A., *ZhOrKh.*, 2015, Vol. 85, No. 3, P. 498. (in Rus.).
- Krysin A. P., Yakovlev O. M., Nikulicheva O. N., Fadeeva V. P., Mater. Vseros. Conf. "O Makromolekulyarnoy Khimii", Ulan-Ude, 2008, P. 70–73. (in Rus.).
- Krysin A. P., Khlebnikova T. B., *ZhOKh.*, 2011, Vol. 81, No. 6, P. 966. (in Rus.).
- USSR Inventor's Certificate No. 1387361, 1987.
- USSR Inventor's Certificate No. 1657517, 1989.
- Krysin A. P., Egorova T. G., Komarova N. I., Vasil'ev V. G., *ZhPKh.*, 2009, Vol. 82, No. 11, P. 1817. (in Rus.).
- Rark S. S., Lee H. J., Jamison A. S., Lee T. R., *ACS Appl. Mater. Interfaces*, 2016, Vol. 8, No. 8, P. 5586.
- Krysin A. P., Yakovlev O. I., *ZhPKh.*, 2013, Vol. 86, No. 7, P. 1064. (in Rus.).
- Andreeva A. I., Sergunova L. I., Dontsov A. A., Osobennosti Stareniya i Zashchita Rezin, Eksploatiruyushchikhsya v Fizicheskikh Agressivnykh Sredakh i v Vakuume, M.: TSNIITeneftkhem, 1988, No. 6, P. 56. (in Rus.).
- Voronchikhin V. D., Gavrikova T. Ya., Goncharov V. M., Bubenev V. A., Bukhtoyarova N. M., *Kauchuk i Rezina*, 2003, No. 1, P. 28. (in Rus.).
- Voronchikhin V. D., Goncharov V. M., Lesik E. I., *Khimiya i Khim. Tekhnologiya*, 2006, Vol. 49, No. 11, P. 42. URL: [http://ctjisuct.ru/files/2006/v49\\_n11\\_2006\\_full.pdf](http://ctjisuct.ru/files/2006/v49_n11_2006_full.pdf) (accessed 10.04.18). (in Rus.).
- Gurvich Ya. A., Privivayushchiesya i Oligomernye Stabilizatory dlya Zashchity Rezinotekhnicheskikh Izdelij Meditsinskogo i Pishchevogo Naznacheniya, M.: TSNIITeneftkhem, 1989. (in Rus.).
- Alshammari H., Miedziak P. J., Davies T. E., Willock D. J., Knight D. W., Hutchings G. J., *Catal. Sci. Technol.*, 2014, Vol. 4, No. 4, P. 908.
- Grassi N., Skott Dzh, Destruktsiya i Stabilizatsiya Polimerov, M.: Mir, 1988, P. 117–128. (in Rus.).
- GOST 9.024–74. Edinaya sistema zashchity ot korrozii i stareniya. Reziny. Metody ispytaniy na stojkost' k termicheskomu stareniyu. URL: <http://gostexpert.ru/gost/gost-9.024-74>; [https://standartgost.ru/g/GOST\\_9.024-74](https://standartgost.ru/g/GOST_9.024-74) (accessed 10.04.18). (in Rus.).