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RESEARCH ARTICLE

# *N*-[(1*RS*)-Camphan-2-ylidene]-4-ethoxyaniline and its reduction product as stabilizers of nitrile butadiene rubbers

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## Abstract

**Objectives.** To investigate the protective efficacy of unreduced and reduced forms of the condensation product of D,L-camphor and *p*-ethoxyaniline in nitrile butadiene rubber formulations when compared with the conventional stabilizer *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine aged under laboratory and *in situ* climatic conditions in the tropics.

**Methods.** The thermostabilizing effect of the condensation product of D,L-camphor and *p*-ethoxyaniline was evaluated by means of infrared spectroscopy using the dynamics of changes in the absorption bands of carbonyl and hydroxyl groups. The features of rubber vulcanization were studied by means of rotorless rheometry. Changes in the physical and mechanical properties of rubbers and degree of cross-linking were evaluated after thermo-oxidative aging in laboratory conditions. They also took into account the results of long-term exposure of samples in undeformed and deformed state in a tropical climate, taking into account meteorological data of the Can Gio climatic testing station.

**Results.** It was found for the first time that condensation products of D,L-camphor and *p*-ethoxyaniline exhibit a stabilizing effect in formulations of rubbers based on polar nitrile butadiene rubber.

**Conclusions.** According to the results of laboratory and *in situ* tests, the study established that the use of *N*-[(1*RS*,2*RS*)-camphan-2-yl]-4-ethoxyaniline (reduced form) as an antifatigue agent is preferable. This is due to the presence of a mobile hydrogen atom at the nitrogen atom. The protective effect is manifested in terms of the better preservation of elastic-strength properties of rubbers with less change in hardness.

## Keywords

condensation product of D,L-camphor and *p*-ethoxyaniline, nitrile butadiene rubber, antifatigue agent, exposure in tropical climate

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НАУЧНАЯ СТАТЬЯ

# *N*-[(1*RS*)-Камфан-2-илиден]-4-этоксианилин и продукт его восстановления как стабилизаторы бутадиен-нитрильных резин

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**Аннотация**

**Цели.** Исследовать эффективность защитного действия невосстановленной и восстановленной форм продукта конденсации D,L-камфоры и *n*-этоксианилина в рецептурах резин на основе бутадиен-нитрильных каучуков в сравнении с традиционным стабилизатором *N*-изопропил-*N*′-фенил-*n*-фенилендиамином, состаренных в лабораторных и натурных климатических условиях тропиков.

**Методы.** Оценку термостабилизирующего влияния продукта конденсации D,L-камфоры и *n*-этоксианилина проводили методом инфракрасной спектроскопии по динамике изменения полос поглощения карбонильных и гидроксильных групп. Особенности вулканизации резин изучали методом безроторной реометрии. Изменение физико-механических свойств резин и степени поперечного сшивания оценивали после термоокислительного старения в лабораторных условиях, а также по результатам длительной экспозиции образцов в недеформированном и деформированном состояниях в тропическом климате с учетом метеоданных климатической испытательной станции Кон Зо.

**Результаты.** Впервые установлено, что продукты конденсации D,L-камфоры и *n*-этоксианилина проявляют стабилизирующее действие в рецептурах резин на основе полярного бутадиен-нитрильного каучука.

**Выводы.** По результатам лабораторных и натурных испытаний выявлено, что в качестве противостарителя наиболее предпочтительно использование *N*-[(1*RS*,2*RS*)-камфан-2-ил]-4-этоксианилина (восстановленная форма), что связано с наличием подвижного атома водорода при атоме азота. Защитный эффект проявляется в лучшем сохранении упруго-прочностных свойств резин при меньшем изменении твердости.

**Ключевые слова**

продукт конденсации D,L-камфоры и *n*-этоксианилина, бутадиен-нитрильный каучук, противостаритель, экспозиция в тропическом климате

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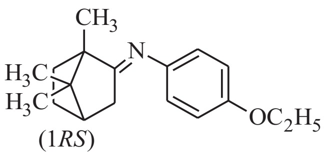
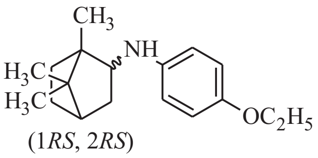
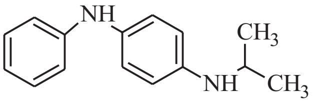
## INTRODUCTION

Rubbers based on nitrile butadiene rubber (NBR) are most common in the manufacture of oil and gas resistant rubber products. However, NBR-based rubbers are prone to structuring under conditions of high temperatures due to the presence of acrylonitrile links in macromolecules. Due to the relatively high unsaturated nature of macromolecules, the materials possess insufficient resistance to various types of aging [1]. Altogether, this leads to an increase in hardness, loss of elasticity and deterioration of rubber properties in general [2].

In order to resolve this problem, stabilizers of different nature are used. The most widely used as thermostabilizers are spatially hindered amines, for example, *N*-phenyl-*N*′-isopropyl-*n*-phenylenediamine (Diafen FP, IPPD); oligomer of 2,2,4-trimethyl-1,2-dihydroquinoline (Acetonanil P); *N*-phenyl-2-naphthalenamine (Naftam-2); *N*,*N*′-diphenyl-*n*-phenylenediamine (Diafen FF), etc. [3]. At the same time, the above-listed amines do not fully meet modern sanitary and hygienic standards. It should also be noted that the protective effect of their use is insufficient, especially under conditions of complex influence of climatic factors on rubber.

**Table 1.** Structural formulas and codes of substances used in rubber formulations

| Structural formula | Name of substance | Code of substance |
|---|---|---|
|  | *N*-[(1*RS*)-Camphan-2-ylidene]-4-ethoxyaniline | Product **I** |
|  | *N*-[(1*RS*)-Camphan-2-yl]-4-ethoxyaniline | Product **II** |
|  | *N*-Isopropyl-*N′*-phenyl-*p*-phenylene diamine (IPPD) | IPPD (comparison sample) |

This determines the need to search for new effective and low-toxic stabilizers. The condensation products of camphor and aniline and their reduction products are of considerable interest in this respect. The first information on the use of substances obtained by the interaction of camphor with aromatic amines in the formulation of natural rubber-based rubbers is provided in US patent No. 2211629 [4]. The synthesis of new compounds of this type is described in [5–8]. Furthermore, there is data on the possibility of using camphor anilines and their reduction products as antimicrobial [9] and antiviral medical preparations [10].

Earlier in [11], we investigated the effect of *N*-[(1*RS*)-camphan-2-ylidene]-2-methylaniline, *N*-[(1*RS*)-camphan-2-ylidene]-2-ethylaniline and *N*-[(1*RS*)-camphan-2-ylidene]aniline on the properties of NBR-based rubbers, including the evaluation of their efficiency as thermal stabilizers. At the same time, a pronounced stabilizing protective effect was not revealed, due to the absence of a hydrogen atom at the nitrogen atom in the unreduced form of camphor anilines [12]. Taking this circumstance into account, the reduced form of *N*-[(1*RS*)-camphan-2-ylidene]-4-ethoxyaniline was synthesized.

The aim of this study was to evaluate the protective effect of the unreduced and reduced form of the condensation product of D,L-camphor and *n*-ethoxyaniline in BPA-based rubber formulations, when compared to the conventional stabilizer *N*-isopropyl-*N′*-phenyl-*n*-phenylenediamine aged under laboratory and *in situ* climatic conditions in the tropics.

## MATERIALS AND METHODS

NBR vulcanizates of BNKS-40 AMS grade with mass fraction of bound acrylic acid nitrile 36–40% (TU 38.30313-2006) were used as objects of the study. An effective vulcanizing system including sulfur donors thiuram D and dithiomorpholine (China) was used for vulcanization. Table 1 presents the structural formulas of the D,L-camphor aniline used and its reduction product synthesized by the authors of this paper. The other ingredients of rubber compounds are given in Table 2.

The following compounds were used as antifatigue agents of rubber mixtures: *N*-[(1*RS*)-camphan-2-ylidene]-4-ethoxyaniline (**I**), *N*-[(1*RS*,2*RS*)-camphan-2-yl]-4-ethoxyaniline (**II**), obtained according to known methods [6, 7]. Diafen FP (Russia) was also used as a substance of comparison. The content of basic substances was ≥98.5%. The synthesis of functionalized D,L-camphor derivatives was carried out according to Scheme 1.

Laboratory rollers Lb 320/160/160 (*POLYMERMASH*, Russia) were used to produce the blends. Rubber without a stabilizing agent is hereinafter referred to as base rubber.

Vulcanization characteristics were studied using an MDR 3000 Professional rotorless rheometer (*MonTech*, Germany) in accordance with GOST 34751-2021[1].

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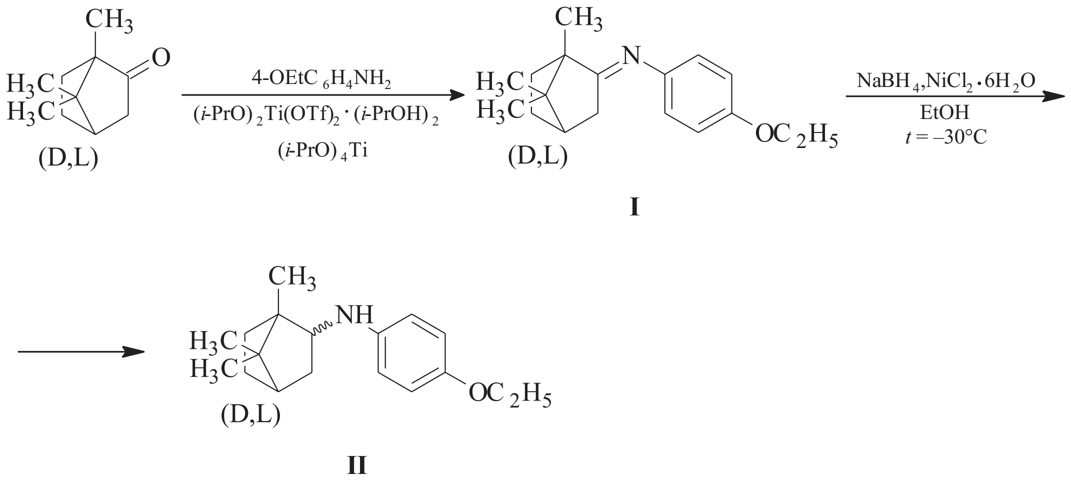
[1] GOST 34751-2021. Interstate Standard. Rubber mixtures. Determination of vulcanization characteristics using rotorless rheometers. Moscow: Russian Institute of Standardization; 2021. https://docs.cntd.ru/document/1200181424?ysclid=lteg4izk40725865149. Accessed November 06, 2023.

**Table 2.** Rubber formulations

| Component | Formulation code | | | |
|---|---|---|---|---|
| | 0* | **I** | **II** | IPPD |
| | Ingredient content, parts by wt | | | |
| Nitrile butadiene rubber BNKS-40 AMN | 100 | 100 | 100 | 100 |
| Carbon black P-234 | 40 | 40 | 40 | 40 |
| Carbon black P-803 | 20 | 20 | 20 | 20 |
| Tetramethylthiuram disulfide | 2.5 | 2.5 | 2.5 | 2.5 |
| Dithiodimorpholine | 1.5 | 1.5 | 1.5 | 1.5 |
| Sulfenamide C (*N*-cyclohexyl-2-benzothiazole-sulfenamide, CBS) | 1.5 | 1.5 | 1.5 | 1.5 |
| Product **I** | – | 2 | – | – |
| Product **II** | – | – | 2 | – |
| IPPD | – | – | – | 2 |
| ZnO | 5 | 5 | 5 | 5 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 |

*0—rubber compound without anti-fatigue agent.



**Scheme 1.** Synthesis of functionalized D,L-camphor derivatives

*In situ* tests of rubber samples at the Can Gio testing station (Ho Chi Minh City, Vietnam) were carried out according to GOST 9.066[2] on deformed samples in the form of strips with the help of clamps, as well as standard plates in their regular state.

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[2] GOST 9.066. State Standard of the USSR. Unified system of corrosion and ageing protection. Vulcanized rubbers. Method of ageing resistance testing under weather conditions. Moscow: Izdatel'stvo standartov; 1994. https://docs.cntd.ru/document/1200015036?ysclid=lteg68jel7692111363. Accessed November 06, 2023.

The physical and mechanical properties of the samples were determined in accordance with GOST 270-75[3] on a 5.0 kN Zwicki-line testing machine (*Zwick/Roell*, Germany). The hardness of rubbers was measured according to GOST 263-75[4]. The assessment of the resistance of rubbers to thermal aging in air environment was carried out in accordance with GOST 9.024-74[5]. Cross-linking density was determined according to the equilibrium swelling method [13].

The study of spectral characteristics in the infrared (IR) range was carried out using an FT-801 Simex IR Fourier spectrometer with a universal attachment of frustrated total internal reflection (FTIR) (*Simex*, Russia), equipped with a diamond element. The spectra obtained were processed in ZaIR 3.5 software[6].

## RESULTS AND DISCUSSION

The features of thermo-oxidative aging of NBR films were preliminarily studied by means of IR spectroscopy in the range of 800–4000 cm$^{-1}$. The rubber was purified from the anti-fatigue agent by re-precipitation using 3% toluene solution with methyl alcohol with further drying until the solvent was completely removed. Products **I**, **II**, and IPPD were added to a 10% solution of rubber in toluene in an amount of 0.25 wt % per rubber. After removing the solvent and drying to constant weight, film samples of about 100 μm thickness were subjected to aging in a thermal cabinet at 100°C. After a certain time, the IR spectrum was determined using an FTIR attachment with a diamond crystal. The process was monitored by the change in the absorption bands at 1720 and 3615 cm$^{-1}$ corresponding to carbonyl (–C=O) and hydroxyl (–OH) groups. The results are presented in Figs. 1 and 2.

The dependencies presented in Figs. 1 and 2 show the dynamics of carbonyl and hydroxyl group accumulation, indicating that in the presence of product **II** and IPPD, the oxidative process develops more slowly. Thus, their effectiveness as anti-fatigue agents were tentatively established.

Figure 3 and Table 3 present the results of rheometric studies characterizing the features of rubber vulcanization depending on the type of the used substance.

As can be seen from the results of evaluating the vulcanization characteristics of rubbers, the addition of IPPD has almost no effect on the sub-vulcanization time ($\tau_s$). In turn, the addition of *N*-[(1*RS*)-camphan-2-ylidene]-4-ethoxyaniline and *N*-[(1*RS*,2*RS*)-camphan-2-yl]-4-ethoxyaniline leads to an increase in the sub-vulcanization time from 2.2 min to 3.2 and 3.7 min, respectively. It can be concluded from the slope angle of the rheometric curves that the process rate in the presence of IPPD and products **I** and **II** slightly decreases due to the inhibition of radical reactions occurring during vulcanization. It can also be observed that in the presence of these substances the values of maximum

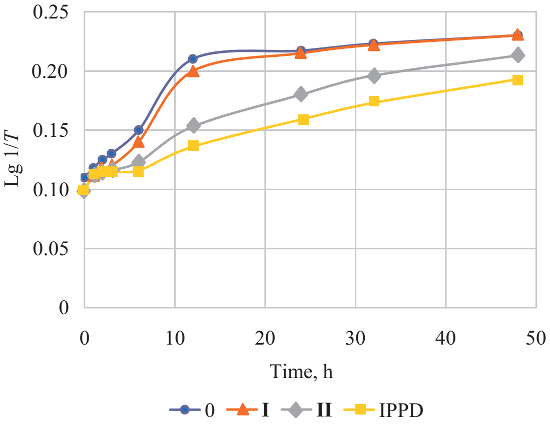

**Fig. 1.** Dynamics of change of intensity of absorption band 1720 cm$^{-1}$(–C=O)

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[3] GOST 270-75. Interstate Standard. Rubber. Method for determining elastic-strength properties under tension. Moscow: IPK Izdatel'stvo standartov; 2008. https://docs.cntd.ru/document/1200018619?ysclid=lteg818rc7736832141. Accessed October 12, 2023.

[4] GOST 263-75. State Standard of the USSR. Rubber. Method for determination of Shore A hardness. Moscow: Izdatel'stvo standartov; 1989. https://docs.cntd.ru/document/1200018610?ysclid=lteg99zuym336475224. Accessed October 12, 2023.

[5] GOST 9.024-74. State Standard of the USSR. Unified system of corrosion and ageing protection. Rubbers. Methods of heat ageing stability determination. Moscow: IPK Izdatel'stvo standartov; 1994. https://docs.cntd.ru/document/1200015022?ysclid=ltegb6r6kl786947653. Accessed September 07, 2023.

[6] https://old.simex-ftir.ru/product_5.html. Accessed September 07, 2023.

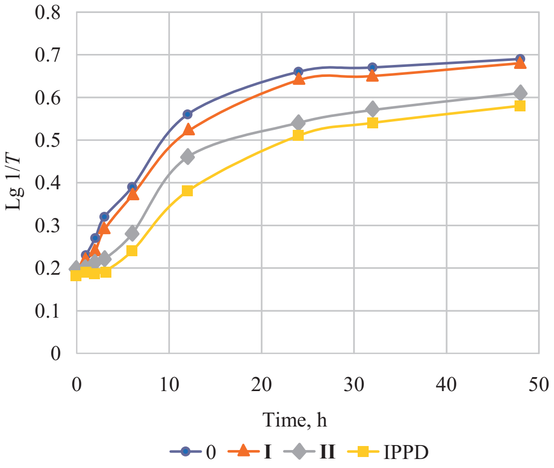


**Fig. 2.** Dynamics of change of intensity of absorption band 3615 cm$^{-1}$(–OH)

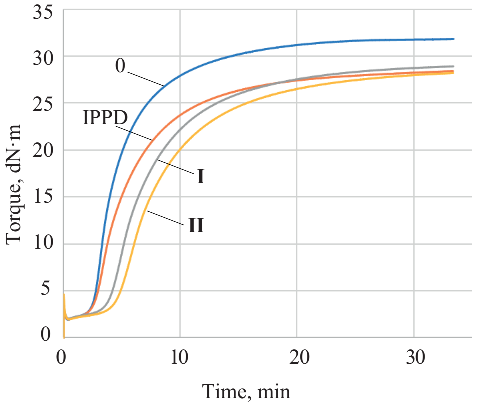


**Fig. 3.** Rheometric curves of vulcanization (*T* = 150°C) of BNKS-40AMN based rubbers

torque are about 3 torque units lower when compared to the base formulation. This indicates a slightly lower degree of crosslinking of these rubbers. Based on these studies, and taking into account the $\tau_{90}$ index (time required to reach 90% of full vulcanization), rubber samples were produced for further laboratory and climatic tests under tropical conditions.

Table 4 shows the results of evaluating the physical and mechanical properties of the rubbers, as well as the level of change in the parameters after laboratory aging at 125°C for 72 h.

Table 5 presents meteorological data for 8 months of natural exposure in the territory of the Can Gio test climatic station.

**Table 3.** Rheometric data of rubber compounds (*T* = 150°C)

| Code | $\tau_s$, min | $\tau_{90}$, min | Minimum torque, dN·m | Maximum torque, dN·m |
|---|---|---|---|---|
| 0 | 2.2 | 11.4 | 1.9 | 31.8 |
| IPPD | 2.3 | 14.5 | 2.0 | 28.9 |
| **I** | 3.3 | 17.4 | 2.0 | 28.9 |
| **II** | 3.7 | 18.0 | 2.0 | 28.1 |

*Note:* $\tau_s$ is the sub-vulcanization time; $\tau_{90}$ is the time required to reach 90% vulcanization.

**Table 4.** Comparative data on the initial properties of rubbers and aged rubbers under laboratory and *in situ* climatic conditions in the tropics

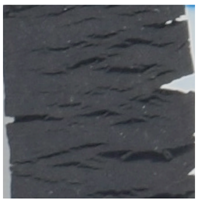
| Rubber code | 0 | **I** | **II** | IPPD |
|---|---|---|---|---|
| Conditional tensile strength, MPa | 26.3 | 25.4 | 26.2 | 26.1 |
| Relative elongation at break, % | 373 | 352 | 364 | 369 |
| Hardness, Shore A units | 74 | 74 | 74 | 74 |
| Degree of cross-linking $\nu \times 10^{-4}$, mol/cm$^3$ | 8.2 | 8.1 | 7.8 | 8.1 |
| Change of properties of rubbers after aging at 125°C, 72 h | | | | |
| Change in conditional tensile strength, % | −37 | −15 | −5 | −3 |
| Change in relative elongation at break, % | −51 | −43 | −31 | −28 |
| Change in hardness, Shore A units | +8 | +4 | +4 | +4 |
| Degree of cross-linking $\nu \times 10^{-4}$, mol/cm$^3$ | 10.3 | 9.6 | 9.3 | 9.2 |
| Changes in properties after 8 months of exposure in tropical climates | | | | |
| Change in conditional tensile strength, % | −29 | −18 | −6 | −11 |
| Change in relative elongation at break, % | −29 | −26 | −11 | −19 |
| Change in hardness, Shore A units | +6 | +4 | +3 | +3 |
| Degree of cross-linking $\nu \times 10^{-4}$, mol/cm$^3$ | 9.5 | 9.4 | 9.1 | 9.0 |

**Table 5.** Meteorological data at the Can Gio climatic testing station for 2022*

| Month | Air temperature, °C | | | Air humidity, % | | | Precipitation, mm | Total solar radiation, MJ/m$^2$ |
|---|---|---|---|---|---|---|---|---|
| | Average monthly | Minimum absolute | Maximum absolute | Average monthly | Minimum absolute | Maximum absolute | | |
| March | 30.3 | 26.1 | 35.7 | 69.6 | 37.3 | 85.7 | – | 680 |
| April | 31.6 | 25.7 | 36.7 | 72.7 | 43.6 | 96.0 | 173.7 | 624 |
| May | 32.0 | 27.0 | 37.8 | 72.1 | 48.0 | 85.8 | 87.4 | 362 |
| June | 30.1 | 24.0 | 38.7 | 76.3 | 49.0 | 94.5 | 136.2 | 513 |
| July | 29.6 | 22.0 | 38.7 | 76.0 | 50.0 | 92.0 | 210.1 | 438 |
| August | 30.3 | 24.0 | 37.6 | 77.1 | 43.0 | 94.1 | 96.8 | 306 |
| September | 30.1 | 24.0 | 36.7 | 76.6 | 53.0 | 91.0 | 287.0 | 391 |
| October | 29.3 | 24.0 | 36.9 | 79.9 | 57.6 | 90.0 | 246.5 | 392 |
| Cumulative* | – | – | – | – | – | – | 633.3 | 3706 |

* 8 months of exposure data.

**Table 6.** Results of climatic tests of rubber samples in deformed state (tensile)

| Rubber code | | 0 | **I** | **II** | IPPD |
|---|---|---|---|---|---|
| Time of appearance of the first cracks on the surface, days | Deformation 10% | 2 | 5 | 7 | 8 |
| | Deformation 20% | 1 | 4 | 2 | 4 |
| Surface photos of rubber strips after 8 months of exposure in a tropical climate | Deformation 10% |  |  |  |  |
| | Deformation 20% |  |  |  |  |

The data shown in Table 4 shows that the presence of a mobile hydrogen atom at nitrogen significantly affects the activity of the substance as an anti-fatigue agent. In particular, if we compare the effectiveness of the unreduced and reduced forms of *N*-[(*1RS*)-camphan-2-ylidene]-4-ethoxyaniline (products **I** and **II**), the best protective effect is observed for samples containing the reduced form. This is manifested in the better preservation of elastic-strength properties, a lower level of change in the hardness and cross-linking degree index both after laboratory and *in situ* tests of samples subjected to the combined influence of tropical atmospheric factors (Table 5). The properties of the base rubber without an anti-fatigue agent change more significantly, as expected. The comparison shows that the protective effect due to the introduction of product **II** is commensurate with the traditional IPPD stabilizer. This, in turn, is consistent with the known theory on the mechanism of action of amine-type anti-fatigue agents [14].

Table 6 shows the results of tropical tests of rubber samples in the deformed state.

As predicted, under test conditions, the first cracks on specimens without anti-fatigue agent were seen in a shorter period of time. When such specimens are stretched in clamps by 10 and 20%, the first cracks form after two and one day, respectively. Rubbers filled with products **I** and **II,** as well as IPPD, show first cracks after 2 to 8 days depending on the degree of deformation. At a relatively low tensile strain (10%), a commensurate protective effect is observed in the cases of product **II** and IPPD.

The photographs presented in Table 6 demonstrate the condition of samples exposed for 8 months in tropical climates under 10 and 20% stretching conditions. The base rubbers (without anti-fatigue agent) are characterized by the presence of larger and deeper cracks regardless of the degree of deformation. A visually different picture can be seen in rubber samples where *N*-[(1*RS*)-camphan-2-ylidene]-4-ethoxyaniline and its reduction product were used. In these cases, the development of the destructive process is much less pronounced, if judged by the number and size of cracks.

## CONCLUSIONS

According to the results of testing of NBR-based rubbers in laboratory conditions and in full-scale climatic tests, it was established for the first time that condensation products of D,L-camphor and *n*-ethoxyaniline exhibit a noticeable stabilizing effect. The use of the reduced form of *N*-[(1*RS*)-camphan-2-ylidene]-4-ethoxyaniline is preferable as an anti-fatigue agent in formulations of NBR-based rubbers, determined by the presence of a mobile hydrogen atom at the nitrogen atom. The protective effect is manifested as the better degree of preservation of elastic-strength properties of rubbers with less change in hardness. In particular, after 8 months of exposure in tropical climate the rubbers display a loss of tensile strength and relative elongation at break by 6 and 11%

respectively. The level of hardness of the materials increases insignificantly, namely by 3 Shore A units. The comparison samples containing *N*-isopropyl-*N*′-phenyl-*n*-phenylenediamine display a loss of tensile strength by 11% and relative elongation at break by 19%.

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## Authors' contributions

**D.A. Nilidin**—conducting experiments in laboratory conditions, analyzing and interpreting the obtained data.

**M.A. Vaniev**—planning and controlling the experiment, data analysis, preparing and editing the text, and approval of the final version of the article.

**A.A. Vernigora**—synthesis of *N*-[(1*RS*)-camphan-2-ylidene]-4-ethoxyaniline and *N*-[(1*RS*,2*RS*)-camphan-2-yl]-4-ethoxyaniline.

**N.A. Salykin**—purification of *N*-[(1*RS*)-camphan-2-ylidene]-4-ethoxyaniline and *N*-[(1*RS*,2*RS*)-camphan-2-yl]-4-ethoxyaniline and sample preparation.

**A.V. Davidenko**—identification of the structure of *N*-[(1*RS*)-camphan-2-ylidene]-4-ethoxyaniline and *N*-[(1*RS*,2*RS*)-camphan-2-yl]-4-ethoxyaniline by physicochemical methods.

**Dang Minh Thuy**—collection, analysis, and statistical processing of meteorological data in the territory of the climate test station, development of methodology of climate tests.

**S.G. Gubin**—designing and conducting the experiment in tropical climate conditions, data analysis.

**I.A. Novakov**—scientific guidance, idea formation, formulation of the aims and objectives of the research.

*The authors declare no conflicts of interest.*

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