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ПОЛУЧЕНИЕ И ИССЛЕДОВАНИЕ ПРОДУКТА ВЗАИМОДЕЙСТВИЯ *ОРТО*-ФЕНИЛЕНДИАМИНА С ЭПИХЛОРГИДРИНОМ В КАЧЕСТВЕ ПРОТИВОСТАРИТЕЛЯ РЕЗИН

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Получен продукт взаимодействия эпихлоргидрина с о-фенилендиамином. Методом обратного титрования показано, что эпоксидные группы были израсходованы в процессе получения аддукта. Инфракрасные спектры регистрировали на Фурье-спектрофотометре FTIR-8400S фирмы Shimadzu. Методом инфракрасной спектроскопии показано, что полученный продукт представляет собой вторичный амин. Таким образом, эпоксидные группы эпихлоргидрина реагируют с аминогруппами о-фенилендиамина. Полученный продукт выделен в виде твердого кристаллического вещества с температурным интервалом плавления 104 – 106 °С. Исследовали резиновые смеси на основе бутадиен-стирольного каучука СКС-30АРКМ-15, содержащие серу, 2-меркаптобензтиазол, дифенилгуанидин, белила цинковые, стеарин технический, технический углерод N-550 и противостарители в дозировке 6,6 ммоль/100 г каучука. В качестве противостарителей применяли продукт взаимодействия эпихлоргидрина и о-фенилендиамина, N-изопропил-N'-фенил-п-фенилендиамин, 2,2-метилен-бис(4-метил-6-третбутилфенол). Параллельно исследовали резиновую смесь без противостарителя. Резиновые смеси изготавливали на вальцах Лб 320 160/160 при температуре 45–55 °С. Вулканизационные характеристики резиновых смесей определяли на реометре Pheo-Line MDR фирмы Prescott Instruments при температуре 160 °С. Установлено, что исследуемый аддукт практически не влияет на скорость вулканизации. Высокие значения разности между максимальным и минимальным значениями крутящего момента резины с исследуемым аддуктом указывали на высокую степень сшивания макромолекул. Вулканизацию проводили в гидравлическом вулканизационном прессе 600-600 2Э при температуре 160 °С в течение 15 мин. Исследования свойств вулканизованных резин проводили согласно принятым для резиновой промышленности стандартам. Высокие значения напряжений при заданных удлинениях резины с исследованным продуктом также свидетельствовали о высокой степени вулканизации. Применение продукта взаимодействия эпихлоргидрина с о-фенилендиамином в составе резин на основе каучука СКС-30АРКМ-15 обеспечивало высокую стойкость к термическому старению и динамическую выносливость.

Ключевые слова: противостаритель, резина, старение, продукт взаимодействия эпихлоргидрина и *о*-фенилендиамина

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REACTION OF *O*-PHENYLENEDIAMINE WITH EPICHLOROHYDRIN AND EVALUATION OF THE PRODUCT AS A RUBBER ANTIAGING AGENT

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The epichlorohydrin - o-phenylenediamine reaction product has have obtained. With reverse titration the fact has been proven that the epoxy groups were completely used up to produce the adduct. The Shimadzu FTIR-8400S Fourier spectrometer was used to register the IR spectra. Through IR spectroscopy it was demonstrated that the resulting product is a secondary amine. Thus, epichlorohydrin epoxide groups react with the o-phenylenediamine amino groups. The product has been isolated in the form of a solid crystalline substance having the melting temperature range of 104-106 °C. The rubber mixes based on SKS-30ARKM-15 butadiene-styrene rubber containing sulfur, 2-mercaptobenzthiazole, diphenylguanidine, zinc white, industrial stearin, N-550 carbon black and rubber anti-aging agents at 6.6 mmol/100 g were also studied. The epichlorohydrin - o-phenylenediamine reaction product, N-isopropyl-N'-phenyl-p-phenylenediamine, and 2,2-methylene-bis(4-ethyl-6-tert-butylphenol) were used as the anti-aging agents. A rubber mix containing no anti-aging additives was studied. The rubber mixes have been prepared in LB 320 160/160 rollers, at 45-55 °C. The vulcanization properties of the rubber compounds were tested using Prescott Instruments Rheo-Line MDR rheometer at 160 °C. It was established that the studied adduct has virtually no effect on the vulcanization rate. High values of the difference between the maximum and minimum values of the torque of rubber with the adduct under study indicated a high degree of cross-linking of macromolecules. The mixture has been vulcanized in a 600-600 2E hydraulic vulcanization press at 160 ºC for 15 min. Studies of the properties of vulcanized rubber were carried out in accordance with the standards accepted for the rubber industry. High tensile stress values at given elongations for the rubber containing the product studied have also indicated a high degree of vulcanization. The use of the epichlorohydrin - o-phenylenediamine reaction product in the SKS-30ARKM-15 rubber based compounds has ensured high thermal aging resistance as well as dynamic fatigue resistance.

Key words: antiaging agent, rubber, aging, *o*-phenylenediamine - epichlorohydrin reaction product

INTRODUCTION

The issues of polymers aging and stabilization as well as those of composite materials are among the high priority areas of polymer science. Oxidation leads to degradation of polymeric materials [1]. The problem of polymers aging along with that of polymeric materials stabilization have been paid great attention in Russia as well as internationally [2]. Polymers/composite materials aging protection is important from a practical

point of view. It is economically feasible to prolong the service life of polymer products through the use of various stabilizers [3-6]. Numerous reports on elastomeric materials aging protection have been presented at various scientific conferences [7-12].

Despite the toxicity of amine-type stabilizers [13-17] and the impossibility of their use for light colored - or multi-colored materials [18], more attention is currently being paid to paraphenylenediamine derivatives as the most effective [18] and the most common [19]. They have proven themselves as good antiaging agents, antifatigue agents, and antiozonants [20-23].

Alkylated derivatives of p-phenylenediamines are widely used in industry. The first step of preparation is obtaining of 4-aminodiphenylamine. The second step is alkylating of 4-aminodiphenylamine with ketones in the presence of catalysts [24]. Thus, the disadvantage of preparation such antioxidants is using two steps.

There are some methods to obtain antioxidants in one step. For example, N,N'-bis(1-methylheptyl)phenylenediamine is obtained by alkylation of phenylenediamine-1,4 with hexylmethyl ketone in the presence of a catalyst. It isn't inferior to N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) as a antioxidant for synthetic rubbers [24]. However, N,N'-bis(1-methylheptyl)phenylenediamine is a reddish brown liquid and can't be used for automatic weighing.

It is known the method to obtain and investigation of amine-containing antioxidants with a hydroxyl group in the molecule. For example, N-phenyl, N'-oxyalkyl-p-phenylenediamine was synthesized and studied in [25]. It has several reactive groups in its structure. The action of each of reactive groups is specific to the deactivation of radicals. Therefore, such substances are effective as rubber antioxidant. Also the presence of hydroxyl groups in its molecule leads to the formation of hydrogen bonds. The hydrogen bonds leads to reducing the leaching and volatile of the antioxidant during the usage of rubber products. However, it is nessesary to use propylene oxide for synthesis. Propylene oxide is toxic and carcinogenic organic compound, a volatile liquid with a low boiling point of 34 °C, extremely flammable. Synthesis requires the use of high pressure.

In this work it was proposed using epichlorohydrin with a boiling point of 117 °C to obtain an antioxidant. Such method wasn't require high pressure.

Currently, new phenylenediamine-derivatives stabilizers are synthesized [25-27] by applying new production methods [28-29].

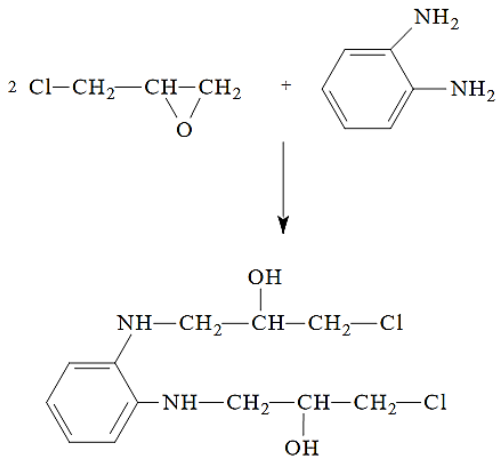
The rubber industry produces and conducts research into not only p-phenylenediamine-based antiaging agents but also into agents on the basis of other aromatic amines to expand the industry's raw material base [30-33].

This paper covers the possibility of obtaining a rubber stabilizer at the epichlorohydrin - o-phenylenediamine reaction. The molecule of obtained antioxidant contains chlorine, which provides a higher molecular weight. Higher molecular weight is important for reducing the leaching and volatile of the antioxidant during the usage of rubber products.

The epichlorohydrin - *o*-phenylenediamine (OPh-E) reaction product has been studied as a part of the styrene-butadiene rubbers.

METHODOLOGY

The OPh-E has been produced through the reaction of epichlorohydrin (as per GOST 12844-74, purity exceeding 99.5%) with o-phenylenediamine (as per Technical Requirements (TR) 6-09-05-1291-84, purity exceeding 97.5%) as shown in the Scheme:



Scheme. Epichlorohydrin - *o*-phenylenediamine reaction
Схема. Реакция эпихлоргидрина - *o*-фенилендиамина

To obtain OPh-E, 0.1 g·mol^{-1} of *o*-phenylenediamine along with 350 ml of acetone have been loaded into the reactor. Upon complete dissolution of o-phenylenediamine, after stirring the boiling reaction mass for 60 min, 0.2 g·mol^{-1} of epichlorohydrin has been added through a drip funnel. Once the complete amount of epichlorohydrin has been introduced, the boiling reaction mass is stirred for 180 min at 56 °C and then cooled. The mass fraction of epoxy groups has been determined through the reverse method (as per GOST R 56752-2015). It has been impossible to register the presence of epoxy groups in the solution as well as within the finished product once the reaction is complete. The reaction mass has been concentrated. The reaction product has been filtered. The obtained product, OPh-E, is a crystalline substance, brown in color,

odorless, having the melting temperature range of 104-106 °C, which range has been determined through the capillary method by using a liquid bath (as per GOST 33454-2015).

The IR spectra of the obtained substance and o-phenylenediamine have been registered with Shimadzu FTIR-8400S Fourier spectrometer.

As an antiaging agent, the OPh-E has been studied within SKS-30ARKM-15 butadiene-styrene rubber (w/w): sulfur – 2.0; 2-mercaptobenzthiazole – 1.5; diphenylguanidine – 0.5; zinc white – 5.0; technical stearin – 1.5; N-550 carbon black – 50.0. Concurrently, we have been studying rubbers with the following anti-aging agents added: IPPD, 2,2-methylenebis(4-methyl-6-tert-butylphenol) (Agidol-2) compared to rubber without additives. The content of anti-aging agents is 6.6 mmol/100 g of rubber. The IPPD was used as a comparison object because of it using for all rubber parts of tires in Russia. [34]. The rubber mixes have been prepared in LB 320 160/160 rollers, at 45-55 °C.

We have tested the vulcanization properties of the rubber compounds by using Prescott Instruments Rheo-Line MDR rheometer at 160 °C (as per GOST 12535-84). We have determined the vulcanization start time t_{s1}, the optimal vulcanization time t_{90}, the minimum M_L and maximum M_{HR} torques.

The mix has been vulcanized in a 600-600 2E hydraulic vulcanization press at 160 °C for 15 min. The rubbers' tensile stress properties (nominal tensile strength f_z, relative elongation at rupture ε, stress at 100% elongation f_{100} and stress at 300% elongation f_{300}) have been determined with the RMI-60 tensile testing machine as per GOST 270–75. Rubber tear strength T_s has been tested with the RMI-60 tensile testing machine on C-shaped undercut samples (G method) as per GOST 262–93. The rubbers' multiple stretching fatigue life N at constant strain amplitude has been determined with the MRS – 2 machine as per GOST 261–79. The strain amplitude value ε_0 is 100%.

The rubbers' thermal degradation resistance has been tested as per GOST 9.024–74. The test result has been considered the change in a characteristic index value upon strength aging S_{fz}, by relative elongation S_ε and by stress at 100% elongation S_{f100}. Thermal aging of the rubbers has been carried out at 100 °C for 72 h.

RESULTS AND DISCUSSION

The o-phenylenediamine IR spectrum (Fig.) demonstrates two absorption bands of 3400 cm^{-1} and 3303 cm^{-1} corresponding to the valence oscillations of the primary aromatic amine.

There is a 3302 cm^{-1} absorption band in the OPh-E 3500-3300 cm^{-1} IR range, which corresponds to valence oscillations of the secondary aromatic amine, the 3400 cm^{-1} absorption maximum, characteristic of o-phenylenediamine, has not been detected. Thus, the epichlorohydrin - o-phenylenediamine reaction forms a secondary amine [35, 36].

The use of Agidol-2 and IPPD in styrene-butadiene rubbers (Table 1) leads to an increase in the optimal vulcanization time t_{90} and the vulcanization start time t_{s1}. OPh-E has practically no effect on vulcanization kinetics.

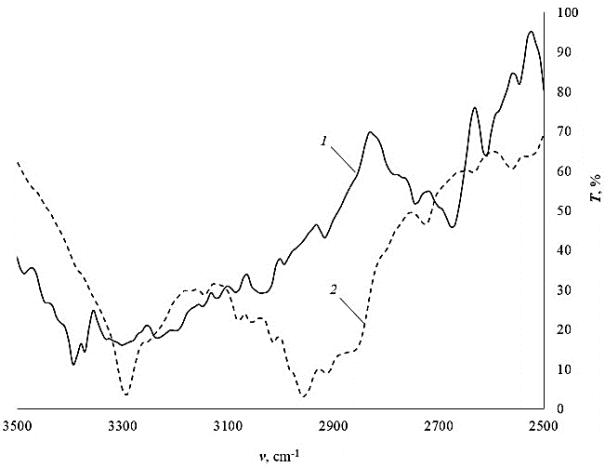


Fig. IR spectra of (1) *o*-phenylenediamine and (2) *o*-phenylenediamine - epichlorohydrin reaction product. T – transmittance (%), ν – wavenumber (cm^{-1})

Рис. ИК спектры *o*-фенилендиамина (1) и продукта реакции *o*-фенилендиамина с эпихлоргидрином (2). Т – пропускание (%), ν – волновое число ($см^{-1}$)

Table 1

Properties of rubber mixtures

***Таблица 1.* Свойства резиновых смесей**

Index	Anti-aging agent			
	OPh-E	IPPD	Agidol-2	-
t_{s1}, min:s	0:29	0:47	1:04	0:39
t_{90}, min:s	5:05	7:37	9:53	4:48
M_L, N·m	1.85	1.78	1.69	1.60
M_{HR}, N·m	17.11	17.09	16.47	15.49
M_{HR} - M_L, N·m	15.26	15.31	14.78	13.89

Based on increacing the stress values at 100% elongation f_{100} and 300% elongation f_{300} the investigated rubbers stand in such line of chemical cross-linking degree Agidol-2< without additive < IPPD < OPh-E (Table 2). Thus, it should be note a high degree of chemical crosslinking of rubber containing the experimental product, OPh-E. Also the high difference between the maximum and minimum torque values (M_{HR} - M_L) for rubbers both with IPPD and OPh-E has indicated to a partial correlation of this parameter with the degree of chemical crosslinking of rubber. The conditional tensile strength f_z and tear resistance T_s of the

studied rubbers are at the same level within the measurement error limit. High fatigue life values at multiple stretching *N* of IPPD and OPh-E rubbers should be noted. The marginal fatigue endurance *N* advantage of IPPD rubber over OPh-E rubber is possibly due to the fact that IPPD rubber has lower stress values at given elongations and higher elongation and is thus lower modulus rubber containing OPh-E. In the constant strain amplitude test mode, the fatigue endurance under repeated tension is higher for low-modulus rubbers.

Table 2

Properties of rubbers
***Таблица 2.* Свойства резин**

Index	Antiaging agent			
	OPh-E	IPPD	Agidol-2	-
f_z, MPa	15.1	15.5	14.4	14.1
f_{100}, MPa	4.7	3.9	3.4	4.4
f_{300}, MPa	13.7	13.1	11.4	12.7
ε, %	360	400	380	330
Ts, kN/m	49	48	50	49
N, thousand cycles	8.5	10.3	6.2	1.8
β	7,07	6,66	6,53	6,28

Table 3

Changes in rubber characteristics after aging
***Таблица 3.* Изменения характеристик резин после старения**

Index	Antiaging agent			
	OPh-E	IPPD	Agidol-2	-
S_{fz}, %	-3	-3	-5	-9
S_{ε}, %	-25	-35	-34	-38
S_{f100}, %	19	36	35	37

In terms of resistance to thermal aging (Table 3), rubbers with OPh-E are not inferior to rubbers with IPPD and are superior to rubbers with Agidol 2.

CONCLUSIONS

Thus, a product of the interaction of epichlorohydrin and o-phenylenediamine was obtained in one step under mild conditions at 56 °C and atmospheric pressure. The reaction product is a solid crystalline substance with a melting temperature range of 104-106 °C.

It has been established that rubber based on SKS-30ARKM-15 with the studied product is not inferior to rubber with N-isopropyl-N'-phenyl-p-phenylenediamine in terms of resistance to thermal aging and is superior to rubber with 2,2-methylene-bis (4-methyl-6-tert-butylphenol). It is shown that the use of the product of the interaction of epichlorohydrin and o-phenylenediamine provides high fatigue endurance under repeated stretching of the studied rubbers.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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