The Influence of Phenolic Antioxidants on the Physical-Mechanical Properties of Hydin T6000-Based Rubber under Climatic Factors and Hydrocarbon Environments

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Abstract. The effectiveness of the stabilizing effect of sterically hindered phenolic antioxidants of the pilot production of N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry (NIOCH SB RAS): CO-3, CO-4, and Stafen, were investigated under climatic conditions of the Republic of Sakha (Yakutia). Rubber samples containing phenolic antioxidants were aged in air, industrial oil of I-50A grade, and oil of the Talakanskooy field for 2 years. The physical-mechanical properties of rubbers based on Hydin T6000 were studied and it has been established that phenolic antioxidants are more effective than the commercial 6PPD antioxidant.

1. Introduction

Elastomer materials can undergo aging, which leads to the destruction of the material at each stage of existence: during the production, operation, and storage [1]. The tendency to aging is a significant drawback for many elastomers, which results in deteriorated quality and reduced product life. Destruction can be caused by mechanical stresses and the action of light, heat, moisture, ozone, oxygen. Under the influence of these factors, there is a process of chain reduction due to the destruction of S-S bonds and the formation of free radicals, which, in turn, contribute to the further destruction of molecules [2]. The intensive development of technology demands reinforced requirements for elastomer materials to increase performance and preserve the original properties in a wider temperature range.

Antioxidants (AO), special stabilizing additives, are introduced into the composition of rubber compounds to increase the resistance to aging. Among them, sterically hindered phenolic antioxidants are highly effective since they capture free radicals and form more stable bonds with them, preventing further destruction of the carbon chain. They are practically inert concerning the oxygen and ozone [3]. Basically, the effectiveness of phenolic antioxidants is determined by the stability of the phenoxyl radical (ArO•). The stability of ArO• is determined by the combination of thermodynamic and kinetic factors [4]. Thermodynamic stability implies low conversion energy of phenol (ArOH) to ArO• and is associated with the delocalization of the spin density of an unpaired electron on an aromatic ring. Kinetic stability of ArO• occurs when there are substituents in the aromatic ring. These substituents create steric barriers to reactions at carbon atoms that concentrate the density of an unpaired electron on an aromatic ring. Kinetic stability of ArO• increases when there are substituents in the aromatic ring. These substituents create steric barriers to reactions at carbon atoms that concentrate the density of an unpaired electron on an aromatic ring. Kinetic stability of ArO• increases when there are substituents in the aromatic ring.
corresponding to them [5-6]. Thus, the behavior of phenoxyl radicals in reactions and the rate of their destruction, in particular, determine the total efficiency of sterically hindered phenolic antioxidants [7-8] and allow preserving the physical-mechanical properties of materials for a long time. The above said proves the effectiveness of the active introduction of these antioxidants in the industry.

The present work is aimed to study the stabilizing effect of new phenolic antioxidants in the pilot production of the NIOCH SB RAS in the climatic conditions of the Republic of Sakha (Yakutia).

2. **Objects and methods of research**

Hydrin T6000 epichlorohydrin rubber with a glass transition temperature of minus 60 °C and high resistance to oils and fuels was selected to investigate the influence of antioxidants on the climatic stability of rubbers. The rubber composition included the following: rubber, sulfur, zinc oxide, magnesium oxide, captax, tiuram, N774 carbon black, stearic acid, dibutyl sebacinate, antioxidant.

Sterically hindered phenolic antioxidants of the pilot production of the NIOCH SB RAS were used as antioxidants: Stafen – di- (2,6-di-tert-butyl-4- (3-hydroxypropyl) phthalate, CO-3 – di- (2,6 di-tert-butyl-4- (3-hydroxypropyl)) sulfide, and CO-4 – di- (2,6-di-tert-butyl-4- (3-hydroxypropyl)) disulfide. 6PPD amine stabilizer, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (China), widely applied in the rubber industry was used to compare the properties. Antioxidants were added to the rubber mixture in an amount of 1 part by weight per 100 parts by weight of rubber. Vulcanization of the samples was performed at a temperature of 155 °C for 20 min.

Samples were exposed in air, as well as in an unheated room in an environment of I-50A industrial oil and oil of the Talakansky field from July 2017 to July 2019. Such parameters as relative tensile strength and elongation at break were determined according to GOST 27075. The change in physical-mechanical parameters was calculated according to GOST 9.066-76 by the formula:

\[ \Delta S = \frac{A_1 - A_0}{A_0} \times 100, \]

where \( A_0 \) is the indicator value before aging, \( A_1 \) is the indicator value after aging.

3. **Discussion of the results**

Figure 1 demonstrates the test results obtained after exposing the samples in the air.
Figure 1. Changes in the physical-mechanical properties of rubbers based on Hydrin T6000 during air exposure.

It is seen that significant changes in the parameters are observed in April and July when the ultraviolet radiation is highly intensive. The processes of additional structure formation proceed in the winter months, which is proved by a slight increase in indicators [9]. Regardless of the exposure duration, rubber with Stafen is characterized by better retention of properties compared to rubbers containing other antioxidants. The greatest change in nominal strength and relative elongation is observed in the summer and amounted to $-11.6\%$ and $-29.6\%$, respectively. The changes in other rubbers ranged from $+46.6\%$ to $-35.7\%$. Concerning the Stafen, the demonstration of such properties can be associated with the effect of intramolecular synergism due to the simultaneous presence and favorable spatial arrangement of several functional groups [10-11].

An important property of rubber products is resistance to aggressive working environments. When rubber contacts with aggressive media, diffusion processes occur and can cause irreversible changes in properties due to the weakening of the bond between macromolecules [12]. In this regard, the samples were aged in I-50A industrial oil and oil of the Talakanskoye field in an unheated room. Changes in the physical-mechanical properties of rubber aged in the industrial oil and petroleum environment are shown in Figure 2 and Figure 3.
Figure 2. Changes in the physical-mechanical properties of rubbers based on Hydrin T6000 maintained in I-50A industrial oil.

After aging in the environment of I-50A industrial oil, the parameters of strength and relative elongation of rubbers increase, which can be explained by a slight swelling of the rubbers in this environment. As is known, a small degree of swelling positively influence on the flexibility of chains, which facilitates the favorable orientation of molecules and improve the strength [13-14]. It should also be noted that intensive swelling of rubbers in the summer period cause smaller changes in strength and relative elongation.

Over the entire period of exposure in the industrial oil, rubber that contains Stafen showed the best stability of properties: the most critical change in strength was +12.6 % and -19.5 % in relative
elongation. The change in strength for both unstabilized rubber and rubber with 6PPD amounted to +36.1 % and +33.7 %, and the change in elongation was +20.4 % and +33.3 %, respectively.

Figure 3. Changes in the physical-mechanical properties of rubbers based on Hydrin T6000 maintained in oil environment.

When contacting with petroleum, there is a slight decrease in strength. However, a sharp increase in the relative elongation is observed as well compared to rubbers aged in industrial oil due to a more active plasticizing effect. The analysis of changes in rubber parameters throughout the entire exposure to petroleum has revealed that rubber with CO-4 antioxidant has the best properties: the maximum strength change was -8.6 % and relative elongation was +33.2 %.
4. Conclusion
It has been established that phenolic antioxidants are more effective than the commercial 6PPD antioxidant. The rubber that contains Stafen showed the best retention of properties in the environment of air and I-50A industrial oil, regardless of the exposure duration. The rubber with CO-4 antioxidant demonstrated the best stability in the petroleum environment. The improved stabilizing effect of sterically hindered phenolic antioxidants is associated with the pronounced effect of intramolecular synergism.

5. References
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