Effect of Production Technology of Hydrin T6000 Elastomers on Their Properties and Structure

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Abstract. The influence of the technology for producing elastomer materials based on epichlorohydrin rubber of Hydrin T6000 brand on physical-mechanical properties, structure formation, and frost resistance is studied. Differences in the properties of vulcanizates are revealed due to the formation of various sulfide bonds in a vulcanization network with different densities. The use of rubber swelling technology in a plasticizer leads to a screening effect, which reduces the interaction of the filler with the polymer. On the plus side, this effect improves low-temperature properties, and on the minus side, deteriorates physical-mechanical properties of the material.

1. Introduction
Sealing devices (sealing rubber) ensure reliable operation of any machinery and equipment as they are widely used in movable and fixed joints to separate structures with different physical properties and (or) parameters. They determine the equipment quality, as well as permissible areas of their application. Incorrect choice of sealing types, their low quality, and improper application can lead to the inaccurate performance of machines, a decrease in their reliability, and large economic losses. In the cold climatic conditions specific for the Arctic zone of the Russian Federation, the operation of the equipment entails great difficulties due to the unique climatic factors and severe road conditions (sandy, gravel roads, etc.). It requires adaptation to the existing extreme climatic and operational conditions. The applied sealing elastomeric materials intended for the operation in cold climatic conditions must have high frost resistance and high resistance to exposure to the operating environment.

Epichlorohydrin rubber (ECHR) is a promising rubber for operating at low temperatures and in aggressive environments due to the presence of polar chlorine atoms, which ensure resistance to the action of oil products and oils, as well as simple ether bonds, and help to maintain the flexibility and elasticity of materials at low temperatures \cite{1}. Nevertheless, aside from choosing the proper elastomeric base, it is necessary to use various prescriptions and technological methods to obtain rubbers with the required properties. One of the important prescription factors for increasing the frost resistance of rubbers is the correct choice of a vulcanizing system, which can affect the degree of density of the spatial grid, as well as the rate of a slowdown of crystallization processes for crystallizing rubbers. However, the most effective way to improve the frost resistance of rubbers is the use of plasticizers, which are low molecular weight substances that change the viscosity of the system, the flexibility of molecules, and the mobility of supramolecular structures. The choice of type, content, and introduction technology of plasticizers largely determines the effectiveness of their action. In this regard, the present work is aimed...
to study the effect of various vulcanizing systems and introduction technology of plasticizer on the structure and properties of vulcanizates based on Hydrin T6000.

2. Research objects and methods
The effect of the vulcanizing system, as well as the method of introducing plasticizers, on the properties and structure of the vulcanizate, is investigated. The frost-resistant rubber of Hydrin T6000 brand by Zeon Corporation (USA, Japan) with a glass transition temperature of 60 °C is used as the elastomeric base. At the first stage of the study, double accelerator systems were used as vulcanization accelerators: thiuram-captax and guanidine-altax in the ratio of 1 and 0.5 pts.wt. per 100 pts.wt. rubber. The rubber compounds also included the following components, pts.wt.: sulfur; N550 carbon black; zinc oxide; magnesium oxide; stearic acid; dibutylsebacate and 6PPD. At the second stage of the study, the rubber compounds contained a thiuram system of accelerators with the presented ingredients, but dioctylsebacate was used as a plasticizer (LLC NIOST SIBUR, Tomsk, Russia).

The mixtures were made by mixing on Sm350 150/150 roll for 30 minutes. Vulcanization of the research samples was performed on a 100-400 2E vulcanization press at a temperature of 155°C for 20 minutes.

Vulcanization (GOST 12535-84) and viscoelastic characteristics were investigated using RPA2000 Alpha Technologies rubber processing analyzer. The parameters of the spatial grid of rubbers were determined by the Flory-Rener equation based on equilibrium swelling in toluene at a temperature of 30°C [2-3]. The study of vulcanizate properties was accomplished according to the standard methods: physical-mechanical properties were determined on UTS-20K universal testing machine according to GOST 270-75; resistance to abrasion was studied on AR-40 machine according to GOST 23509-79; resistance to the effects of liquid aggressive environments in an unstressed state was investigated according to GOST 9.030-74 at a temperature of 70 °C for 24 hours; frost resistance under tension was according to GOST 408-78.

3. Discussion of research results
Table 1 shows the results of a study of the vulcanization characteristics of rubber compounds, indicators of the spatial grid of rubbers and their physical-mechanical properties.

It is demonstrated that different systems of accelerators have different effects on the vulcanization characteristics of rubbers. Thus, vulcanizates with the thiuram-captax system have the highest values of torque and provide faster beginning and optimum of vulcanization compared to vulcanizates with the guanidine-altax system.

The results of the study of spatial grid indicators revealed that vulcanizates with the first system of accelerators are characterized by an increased number of cross-links, a correspondingly higher density of the vulcanization network and a lower molecular weight of the chain segment between two cross-links. This can be explained by the fact that thiurams are prone to the formation of shorter mono- and disulfide cross-links in the spatial grid during vulcanization. Whereas, guanidines predominantly lead to the formation of longer polysulfide cross-links, which is confirmed by the data of the spatial grid [4, 5]. Vulcanizates with the guanidine-altax system are characterized by a higher molecular weight of the chain segments, fewer cross-links and a less solid density. The spatial grid data correlate with the results of studies of the elastic-strength characteristics of rubbers. Thus, both vulcanizates with different vulcanization systems demonstrated the same level of relative tensile strength. However, rubber with the first accelerator system is characterized by higher relative stress at 100% elongation and lower relative elongation compared to rubber with a guanidine accelerator system, which is explained by the different structure of the forming cross-links. Wear and oil resistance of both vulcanizates are at the same level. The results of the study of frost resistance showed high frost resistance of rubbers at a temperature of minus 55°C. Herewith, rubber with a thiuram vulcanization system is characterized by the highest coefficient of frost resistance. It can be assumed that precisely the presence of such a degree of mesh density ensured its high frost resistance since an increase in the frost resistance can occur until a certain critical thickness of the vulcanization network density is reached [6].
Table 1. Properties of rubbers based on Hydrin T6000.

| Vulcanization characteristics of rubber compound at a temperature 155°C, strain amplitude 6.98% и frequency 1.67 Hz | ML, kPa | MH, kPa | t<sub>s</sub>, min | t<sub>90</sub>, min |
|---|---|---|---|---|
| T6000+ «thiuram-captax» | 124.73 | 1772.03 | 2.47 | 6.14 |
| T6000+ «guanidine-altax» | 107.18 | 988.48 | 5.71 | 13.50 |

| Parameters of the spatial grid of rubbers |
|---|---|---|---|---|
| | Q<sub>q</sub>, % | ν·10<sup>4</sup>, mole/cm<sup>3</sup> | М<sub>c</sub>, kg/mole | n·10<sup>-19</sup> |
| T6000+ «thiuram-captax» | 2.58 | 1.43 | 7510.5 | 8.5 |
| T6000+ «guanidine-altax» | 3.38 | 1.00 | 10603.9 | 6.0 |

| Physical-mechanical properties of rubbers |
|---|---|---|---|---|
| | f<sub>p</sub>, MPa | f<sub>100</sub>, MPa | ε<sub>p</sub>, % | ∆V, cm<sup>3</sup> | ∆Q, % | K<sub>m</sub> at IRM901,-55 °C |
| T6000+ «thiuram-captax» | 10.2 | 5.8 | 200 | 0.066 | -0.32 | 0.453 |
| T6000+ «guanidine-altax» | 10.5 | 3.5 | 471 | 0.059 | -0.31 | 0.229 |

Note: Примечание: ML, kPa – minimum torque; MH, kPa – maximum torque; t<sub>s</sub>, min – scorch start time; t<sub>90</sub>, min – optimum vulcanization time; Q<sub>q</sub>, % - equilibrium degree of swelling; ν·10<sup>4</sup>, mole/cm<sup>3</sup> - crosslink density; М<sub>c</sub>, kg/mole - molecular weight of a mesh chain segment; n·10<sup>-19</sup> - the number of cross-links in 1 cm<sup>3</sup> of vulcanizate; f<sub>100</sub>,MПа - conditional stress at 100% elongation; f<sub>p</sub>, MПа – conventional tensile strength; ε<sub>p</sub>, % - elongation at break; ∆Q, % - degree of swelling; ∆V, cm<sup>3</sup> – объемный износ при абразивном истирании; K<sub>m</sub> - coefficient of frost resistance in tension.

Figure 1 shows the results of the viscoelastic characteristics of vulcanizates for the in direct assessment of the structure of the materials under study. The dynamic loading mode of vulcanizates is as follows: frequencies are from 0.1 to 20 Hz, the temperature is 100 °C and a strain amplitude is 13.96%. The rubber compounds were subjected to the determination of volcanic characteristics before the test with the following cooling of the samples to the desired temperatures.

The influence curve of the storage modulus G’ and the loading frequency (1a) shows that the value of both vulcanizates gradually increases with increasing load frequency. It is explained by the improved resistance to cyclic effects of cross-linked vulcanizates. Moreover, vulcanizates with a thium system of accelerators over the entire frequency range are characterized by higher G’ values compared to vulcanizates of the guanidine system of accelerators. This indicates a denser vulcanization network in the first vulcanizate [2, 7, 8].
Figure 1. Dependence of the storage modulus ($G'$, a), loss modulus ($G''$, b), and the mechanical loss tangent ($\tan \delta$, c) of rubbers based on T6000 on the loading frequency.

Different influence curves of the loss modulus ($G''$) and the tangent of mechanical loss ($\tan \delta$) of vulcanizates demonstrate the different structure of the cross-links formed when using the thiram and guanidine systems of accelerators (1 b, s). The values of $G''$ and $\tan \delta$ of vulcanizates with a thiram system of accelerators, in which less mobile mono- and disulfide cross-links are formed, increase before reaching a frequency of about 1 Hz with the following sharp decline. It can be explained by the fact that their macromolecules are less subject to conformational changes. Vulcanizates with more mobile polysulfide cross-links manage to respond to external cyclic effects and to rebuild. This leads to a gradual increase in $G''$ and $\tan \delta$ of vulcanizates with a guanidine system of accelerators as the loading frequency increases.

Further, the influence of the plasticizer introduction technology on the structure and properties of rubber is investigated. It is known that plasticizers form an important class of functional ingredients of rubber compounds that have the greatest potential for improving the frost resistance of rubbers. Plasticizer introduction was performed in two technological ways:
- 1st method: all the ingredients of the rubber compound were introduced sequentially according to the mixing chart;
- 2nd method: the rubber was previously swollen in a plasticizer for 48 hours at 23 °C, the remaining ingredients were introduced afterwards according to the mixing chart.

Table 2 presents the physical-mechanical and low-temperature properties of the obtained materials.
Table 2. Physical-mechanical and low temperature properties of rubbers.

| Material | \( f_0 \) MPa | \( f_{100} \) MPa | \( \varepsilon_p \) % | \( K_{m-45^\circ C} \) | \( K_{m-50^\circ C} \) | \( \Delta Q_{oil} \) % |
|----------|----------------|-----------------|-----------------|-----------------|-----------------|------------------|
| T6000+ DOS Technology №1 | 11,6 | 4,8 | 337 | 0,71 | 0,53 | 23,18 |
| T6000+ DOS Technology №2 | 9,3 | 4,3 | 280 | 0,83 | 0,62 | 26,67 |

It is shown that rubber previously swollen in the plasticizer is rather inferior in terms of elastic strength and oil resistance. However, the results of low-temperature tests have revealed that it is characterized with significantly high coefficients of frost resistance under tension at -45°C and at -50°C compared to the rubber obtained by the standard technology. The use of the technology of preliminary swelling of rubber in the plasticizer caused the screening effect that reduces the interaction of the filler with a polymer. This led to the improvement of low-temperature properties and the deterioration of the physical-mechanical properties of the material.

The viscoelastic characteristics of vulcanizates were studied on RPA-2000 with the dynamic loading mode at different strain amplitudes (from 0.05° to 20°) and a frequency of 1 Hz at a temperature of 60°C to determine the effect of the technology for introducing plasticizer into the rubber mixture on its properties.

Fig. 2 presents the results of dynamic testing of samples at different strain amplitudes. The dependence of \( G' \) on the strain amplitude demonstrates the uniform distribution of fillers in the rubber. Subsequently, it is possible to evaluate the influence of the production technology of rubber on the performance properties [9].

**Figure 2.** Dependence of \( G'(a) \) and \( G''(b) \) of T6000-based rubbers on the strain amplitude: 1 - vulcanizate with a DOS content according to technology No. 1; 2 - vulcanizate containing DOS according to technology No. 2.

It is shown that at small strain (up to 2 degrees) the \( G' \) values in a rubber sample obtained by standard technology are less than the \( G' \) values of the sample obtained by the technology of rubber swelling in a plasticizer, i.e. the "Payne effect" is dominant in the samples obtained by method No. 1. The lower the change in \( G' \) is, the better the dispersed fillers are distributed in the volume of the elastomeric matrix. A sharp decrease in \( G' \) with increasing strain is associated with a break in the filler-filler links [10-17].
5. References

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