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Study of the Performance of Cold Resistant Sealing Rubbers in Cold Climates

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***Abstract* – An effect of cold climates and hydrocarbon environment on the performance of elastomers based on nitrile-butadiene, epichlorohydrin, propylene oxide, F-4 polytetrafluoroethylene and zeolite paste containing propylene oxide rubbers were studied during 1-2 year full-scale exposure to cold climates in the Republic of Sakha (Yakutia). High stability of the operational parameters of materials based on propylene oxide and epichlorohydrin rubbers after exposure to oil was observed, which is associated with their unique cold resistance. In addition to high frost resistance, they exhibit high ozone, weather and heat resistance up to 150 °C, which makes them a promising material for use in the automotive, oil and mining industries, as well as in other fields of application.**

Keywords – propylene oxide; epichlorohydrin; nitrile-butadiene rubbers; polytetrafluoroethylene; zeolites; climate resistance; full-scale exposure; cold resistance; diffusion processes; sealing rubber.

I. INTRODUCTION

The use of elastomers in northern regions of the Russian Federation is associated with several problems, the main of which is the loss of their performance under severe climatic factors [1, 4, 5]. In winter, elastomer is affected by extremely low temperatures (up to –65 °C), significant (up to 30 °C) variation with the transition through the dew point in the autumn-spring period, and an increased amount of ultraviolet and ozone in the atmosphere [2]. When temperature falls, the elasticity of sealing materials decreases, the probability of transition to the glassy state increases. Temperature drops cause freezing of seals to the parts being sealed, and solar radiation causes destruction and radiation heating [3]. Destruction of elastomer material leads to the failure of machines and mechanisms in general, machine downtime, the cost of enterprises to carry out repair and restoration work [4, 5], which negatively affects the level of economic development in the region. At the same time, the development of the Arctic regions of the Russian Federation remains one of the priorities, which becomes of the state level focus: it is planned to develop the Northern Sea Route, offshore oil production, and improve the infrastructure of the Arctic regions. The development of the northern regions characterized by harsh climatic conditions should be carried using modern technology employing elastomers suitable for use at temperatures down to –60 °C.

Sealing rubber is used to produce a variety of mechanical rubber goods (MRG) applied to seal joints and prevent leakage of the working environment (fuel, oil, lubricants, i.e. hydrocarbon-based substances). MRGs include seals, cuffs, packers and rubber-metal products used in a large number of machines and mechanisms, mine equipment, sea and river vessels, and automobile and pipeline transport [6].

Traditionally, mass production of rubber-based MRGs uses rubber based on butadiene-nitrile rubbers with low content of acrylic acid nitrile (SKN-18, SKN-26), which have a rational balance of "frost resistance–oil and petrol resistance–cost". In the entire family of nitrile butadiene rubbers, SKN-18 shows the lowest oil and petrol resistance, but higher low-temperature elasticity and flexibility, it exhibits glass transition temperature T_g = –50 °C. As the content of nitrile groups increases, oil and petrol resistance grows and frost resistance decreases. Plasticizers significantly increase frost resistance, therefore this method is considered to be one of the most common techniques to improve low-temperature characteristics of nitrile-butadiene rubber [7,13].

Propylene oxide (SKPO) is a new Russian elastomer, which is a copolymer of propylene oxide and allyl glycidyl ether produced in pilot batches in Sterlitamak [7, 8]. Simple highly flexible ether bond in the main chain makes rubber highly frost resistant (glass transition temperature T_g=–74 °C). The glass transition temperature determines the limit of high elastic properties, and the cold resistance coefficient (K_V) is more informative to show whether materials can be used as sealing rubber. For model rubber of sulfuric vulcanization based on SKPO, K_V determined at –50 °C is 0.8–0.9, i.e. the performance of these rubbers at critical (–45÷–55 °C) operating temperatures is expected to be high. Testing of this rubber in cold climates and creation of materials based on the rubber to be reliably used as critical parts of Northern equipment is relevant.

Another new material of considerable interest to study its climatic stability under extreme conditions of the North under the impact of the hydrocarbon environment is the epichlorohydrin rubber Hydrin T6000 (Zeon, Japan). It belongs to the same group of epichlorohydrin rubbers as SKPO [8], and it is a terpolymer composed of propylene oxide, epichlorohydrin and allyl glycidyl ether chains. Tg of the epichlorohydrin rubber is –60 °C, and K_V measured at –50 °C is 0.7. Some deteriorated low-temperature characteristics of epichlorohydrin-based rubber as compared to SKPO, which is observed due to the presence of polar chlorine atoms in epichlorohydrin rubber that reduce flexibility of rubber chains, is compensated by its higher resistance to hydrocarbon media.

Thus, the study investigates the performance of both traditional and new materials based on domestic and foreign special purpose rubbers used for production of MRGs under simultaneous exposure to naturally low temperatures and the hydrocarbon environment.

II. METHODS AND MATERIALS

The whole complex of impacts on the material during product performance cannot be simulated under laboratory conditions. Full-scale climatic tests of rubber most fully characterize the performance of the material. In M.K. Ammosov NEFU, these studies have been conducted for a number of years at the climate range under conditions closest to actual operating conditions. For example, the performance of the model rubber based on propylene oxide rubber [9] was studied in exposure of rubber to oil at ambient temperature.

We have developed several SKPO-based materials that show higher wear and oil resistance compared to the original rubber, for example, rubber containing activated natural zeolites from Yakutsk deposits ([10], RF Patent N2294341, 2007), rubber containing PTFE F-4 and an additive that affects the phase morphology of the mixture – zeolite paste (Patent RF N2294346, 2007). These materials exceeded the initial material in a number of parameters, but in order to test their performance in cold climates, full-scale exposure to the hydrocarbon environment in the climatic conditions of the Republic of Sakha (Yakutia) is required. SKPO-based rubber and 20 phr (parts per hundred rubber) F-4 polytetrafluoroethylene, and rubber of the same composition with 15 phr zeolite paste were taken for full-scale exposure.

Polytetrafluoroethylene F-4 as a component of the developed rubber was chosen due to the unique combination of the properties of PTFE, namely, aggressive media resistance, heat resistance and low friction coefficient. Addition of fluoropolymer in SKPO improved the strength properties, oil resistance, and volumetric wear was reduced by half, however, low-temperature characteristics were deteriorated compared to the initial rubber. Therefore, the method of mechanical activation and joint processing of zeolites [10–12] and dibutyl phthalate in the AGO-2 centrifugal-planetary mill were used to produce an additive intended for directional effects on the interfacial interaction and phase morphology of polymer blends. Its addition into the SKPO-PTFE mixture increased frost resistance to the level of the initial SKPO, decreased compression set by 50% and reduced the degree of swelling.

The composition of rubber based on epichlorohydrin rubber Hydrin T6000 brand included the filler – carbon black, plasticizer – dibutyl phthalate (not more than 10 phr), vulcanization accelerators, antioxidants and sulfur. The rubbers based on butadiene-nitrile rubbers were provided by PJSC Uralsk Plant of Rubber Products (Ekaterinburg) and were compositions based on SKN-18 and SKN-26 containing 10–12% wt. of ester plasticizers.

Previously, we developed a methodology to study changes in rubber properties with simultaneous exposure to the hydrocarbon environment and naturally low temperatures in field tests [9]; we developed a system for comprehensive assessment of the combined effect of the environment and low temperature on rubber properties, which allows us to characterize their performance in cold climates. To assess the performance of rubber samples placed in oil, these were exposed to full-scale exposure for 1–2 years in an unheated warehouse under the climatic conditions of Yakutsk. (monthly average air temperature during this period were close to the long-term average values).

The rubber samples were periodically extracted from oil and tested to determine tensile strength (GOST 270-84), compression set (GOST 9.029-74), cold- resistance coefficient at extension (K_M, GOST 408-78) or elastic rebound after compression (cold-resistance coefficient (elastic recovery coefficient (K_V, GOST 13808-79), and the degree of swelling in the hydrocarbon medium (GOST 9.030-74). All this enabled comprehensive description of the material state, assessment of the degradation changes due to aging under the impact of climatic factors and physically aggressive environment.

III. RESULTS

As we previously stated [9], the interaction of rubbers with the medium is accompanied by a series of diffusion processes associated with both penetration of hydrocarbons into the elastomer material and wash-out of rubber ingredients soluble in the medium [3]. These processes along with the aging of the material under the impact of climatic factors determine the change in the operational performance of materials and products manufactured based on them during full-scale exposure.

During prolonged exposure to oil (2 years) in cold climates, the physical and mechanical characteristics, compression set, and the degree of swelling of epichlorohydrin rubber samples underwent slight seasonal variations associated with changes in ambient temperature, while the values of the main parameters did not go beyond the standard values. Comparison of the results of climatic testing of Hydrin T6000 epichlorohydrin rubber and the data obtained for NBR showed that the low-temperature characteristics of Hydrin T6000 epichlorohydrin rubber remained almost unchanged, whereas the cold-resistance coefficients of NBR that were determined at –50 °C decreased to 0 during the first months of oil exposure (Fig. 1). It should be noted that the critical value of the elastic recovery coefficient K_V, which maintains the tightness of sealing joint, is 0.2 [13]. That is, after 1–2 months of hydrocarbon exposure, all the investigated NBR-based rubber samples will not ensure operational performance of the components at operating

temperatures of –45÷–50 °C, since the elastic recovery coefficient is significantly less than 0.2.

The epichlorohydrin rubber cold-resistance coefficients for elastic recovery remained persistently high throughout the entire period of full-scale exposure, that is, at –50 °C, the elastic recovery coefficients varied from 0.7 to 0.58. The plasticizer content in epichlorohydrin rubber-based rubber was minimal. The plasticizer was actively washed out by the medium, but its absence had practically no effect on low-temperature characteristics of HydrinT6000 epichlorohydrin rubber, since low-temperature elasticity in this case was determined by high flexibility of the polymer base. For BNKS-based rubber, which exhibits high content of plasticizer, its extraction causes critical non-reversible decrease in the elastic recovery coefficient at –50 °C. The addition of significant amounts of plasticizer is one of the most common ways to increase the cold resistance of NBR. This rubber may contain up to 40 phr of plasticizer per 100 phr of rubber [13]. Manufacturers, as a rule, do not consider the operating conditions for MRG and the processes occurring during their contact with the medium. As a result, the actual cold resistance of these goods is much lower than the stated one.

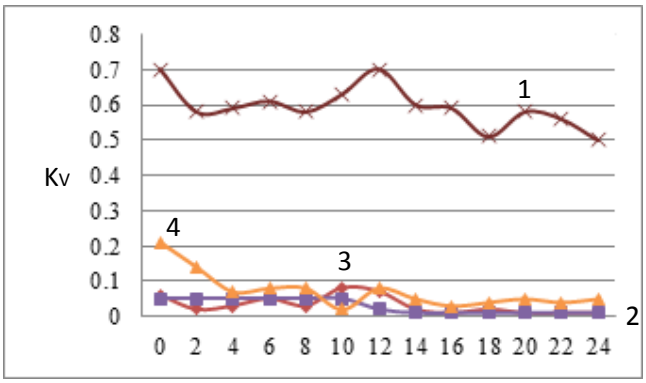

Fig. 1. Dependence of the cold resistance coefficient K_V at –50 ºC for HydrinT6000 epichlorohydrin rubber (1), SKN-26 (2,3), and SKN-26 + SKN-18 (4) samples exposed to oil for 24 months.

As a result of the exposure to oil, Hydrin T6000 epichlorohydrin rubber proved to be suitable for climatic conditions in Yakutsk, and therefore it should be recommended for further use. Comparison of these results with the previously obtained data for SKPO-based rubber [9] showed that general regularities of changes in properties that occur during the exposure to oil remain similar. After exposure, the cold-resistance coefficients for elastic recovery remained high for both SKPO and epichlorohydrin rubber, which is much higher than those for traditional NBR rubber for arctic use. Thus, at–50 °C K_V for SKPO and for epichlorohydrin rubber varied from 0.85 to 0.65 and from 0.7 to 0.58, respectively. When placed in oil at the ambient temperature, the epichlorohydrin rubber samples showed less swelling potential, that is, the absolute values of the degree of swelling in oil were 10÷13%, which is somewhat less than that for SKPO (12÷15%).

In addition to high cold resistance, these rubbers exhibit high ozone and weather resistance (small amount of double bonds in the polymer structure) and heat resistance up to 150 °C. This allows their use to produce MRG for the automotive, petroleum and petrochemical industries, and for the manufacture of the equipment designed for use in cold climates. In addition, these rubbers proved to be appropriate for modification and production of new elastomers with improved properties.

The strength properties of modified SKPO did not change significantly during the exposure. Rubber containing F-4 and zeolite paste was slightly inferior to rubber that did not contain a mineral additive. During exposure, the degree of swelling in SKPO did not exceed 22%. The composition containing zeolite paste was characterized by lower (by 13%) swelling degree parameters due to the adsorption effect of activated zeolites on polymer macromolecules during rubber structure formation [11, 12].

As our studies showed that diffusion processes occurring between the material and the medium have a positive effect on changes in compression set, which is apparently due to some plasticizing effect of petroleum hydrocarbons on rubber (Fig. 2). Low compression set indicates a high degree of material recovery after the exposure, which is especially important for sealing rubber, since the main purpose of sealing is to close gaps and prevent leakage. At the initial stage, rubber containing F-4 shows high compression set values. Due to swelling in the medium and the plasticizing effect of oil, this indicator did not exceed 40% during the exposure versus 60% at its initial stage. After oil exposure, the average compression set values for rubber based on the SKPO/PTFE mixture containing zeolite paste were 11% lower than those for rubber based on the SKPO/PTFE mixture without a mineral additive.

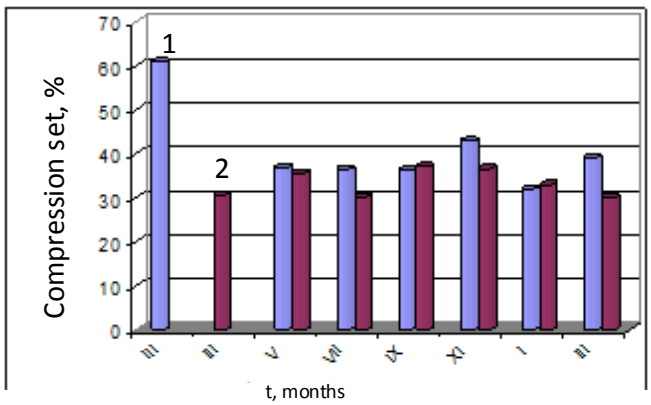

Fig. 2. Dependence of the compression set for SKPO samples exposed to oil for 12 months: (1) SKPO + PTFE; (2) SKPO + PTFE + paste.

As for modified SKPO -based rubber, exposure to oil had little effect on their cold resistance: throughout the entire period of exposure, it exhibited high K_M values at –50 ºC (Fig. 3). Additional introduction of zeolite paste to the elastomer material based on SKPO and fluoroplastic F-4 enabled higher cold resistance of rubber, which was maintained during the exposure. These changes in operational performance are due to the features of zeolitic paste, which affects the level of interfacial interaction in mixed compositions and contributes to better dispersion of fluoroplastic particles in the elastomer matrix. This was evidenced by the studies of the rubber structure using electron microscopy.

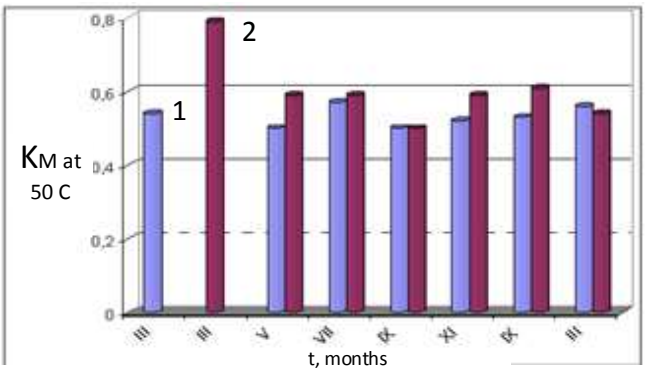

Fig. 3. Dependence of the cold-resistance coefficient at –50 ºC for SKPO samples exposed to oil for 12 months: (1) SKPO + PTFE; (2) SKPO + PTFE + paste.

IV. Conclusion

In cold, sharply continental climates, cyclic temperature changes with a transition through 0 °C twice a day in the spring and autumn periods lead to intensification of diffusion processes. This causes wash-out of plasticizers and a decrease in the cold-resistance coefficient during oil exposure of rubber. This is especially evident for the studied SKN-18 and SKN-26 NBR, whose Tg ranges from –50 to –40 °C. After the first months of exposure, the cold-resistance coefficient of these rubbers at –50 °C irreversibly decreased to 0. Addition of significant amounts of plasticizers to these rubbers does not solve the problem of the cold resistance improvement. For production of sealing rubber, which could reliably be used in extreme climatic conditions of the Republic of Sakha (Yakutia) and other Arctic territories of the Russian Federation, it is preferable to use new materials of the group of epichlorohydrin rubbers – SKPO and epichlorohydrin rubber. Due to the presence of ether bonds in the main chain of elastomers, which provide high low-temperature elasticity, these materials exhibit high values of cold-resistance coefficients and wide operating temperature range.

When exposed to oil, Hydrin T6000 rubber showed excellent low-temperature characteristics. In addition, the tensile strength and compression set did not go beyond the nominal values typical of sealing rubber.

The analysis of the obtained results showed that Hydrin T6000 can be used as a basis for rubbers used for production of sealing parts with increased reliability when operating in cold climates. Another promising rubber for use in arctic conditions is SKPO manufactured in Russia, which exhibits unique cold resistance (Tg=-74 °C). We produced a number of materials based on this rubber, which also proved to be efficient during full-scale exposure.

Our studies into the efficiency of SKPO- and PTFE-based rubber under full-scale exposure to oil showed high stability of operational performance. The composition of SKPO/F-4 containing zeolite paste, in contrast to the composition without paste, is characterized by high degree of stability of the degree of swelling, compression set and cold-resistance coefficient, which indicates its potential for use in polymer mixtures. The mechanism of the effect of zeolite paste requires a detailed study.

V. Acknowledgments

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References

[1] L.L. Grachev, I.S. Filatov, I.N. Chersky, About physicomechanical aspects and methods of testing polymeric materials at low temperatures. Cold resistance of polymeric materials and products. Yakutsk: YAF USSR Academy of Sciences, 1974, pp. 3–9.

[2] M.K. Gavrilova, Climate Central Yakutia. Yakutsk: Yakut Book Publishing House, 1973, pp. 119.

[3] Y.S. Zuev, Failure of Polymers under the Influence of Aggressive Media. Moscow. Chemistry, 1972, pp. 229.

[4] I.S. Filatov, Features of the behavior of polymeric materials and ways to create them for cold climate conditions. Construction polymers at low temperatures. Yakutsk: Yaf Academy of Sciences of the USSR, 1976, pp. 3–15.

[5] I.N. Chersky, V.A. Morov, “Analysis and prediction of rubber and seals serviceability in Arctic conditions”, Kautschuk und Gummi Kunststoffe, vol. 43, no. 6, pp.128–129, 1990.

[6] A.I. Golubev, L.A. Kondakova et al., Seals and Compaction Equipment. Moscow: Engineering, 1986, pp. 463.

[7] O.A. Govorova, A.S. Vishnitsky, G.V.Chubarova, Y.L. Morozov, “Development of weather-resistant rubbers with improved low-temperature and adhesive properties”, Kauchuk I Rezina, no. 2, pp. 18–20, 1999.

[8] A.V. Rumyantseva, V.I. Klochkov, S.K. Kurlyand, M.I. Glushak, G.M. Khvostik, “Features of the structure and properties of rubbers based on cyclic α-oxides”, Materials Science, no. 2 (82), pp. 117–122, 2015.

[9] N.N. Petrova, A.F. Popova, E.S.Fedotova, “Investigation of the influence of low temperatures and hydrocarbon environments on the properties of rubbers based on propylene oxide and nitrile-butadiene rubbers”, Rubber and rubber, no. 3, pp. 6–10, 2002.

[10] N.N. Petrova, J. Lee, V.V. Portnyagina, D.-Y. Jeong, J.-H. Cho, “Antiswelling and Frost-resistant Properties of a Zeolite-modified Rubber Mechanical Seal at Low Temperature”, Bulletin of the korean chemical society. Soc., vol. 36, pp. 464–467, 2015.

[11] N.F. Chelishchev, B.G. Berenstein, V.F. Volodin, Zeolites – A new type of mineral raw materials. Moscow: Nedra, 1987, pp. 176.

[12] T. Bazylakova, D. Ondrusova, M. Pajtasova, S. Lalikova, M. Olsovsky, “Study of zeolites as fillers in the rubber compounds”, In Proceeding sof the 19th Joint Seminar Development of Materials Science in Research and Education”, August 31 – September 4, Zavagna Poruba, pp. 12, 2009.

[13] M.F. Bukhina, S.K. Kurlyand, Low-temperature behaviour of elastomers, Leiden; Boston, VSP, 2007, pp. 157–181.