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INHIBITION EFFICIENCIES OF SODIUM SORBITOLBORATE ON THE CORROSION OF STEEL AND NON-FERROUS METALS IN COOLING MEDIA

NĀTRIJA SORBITOLBORĀTA PIELIETOŠANA TĒRAUDA UN KRĀSAINO METĀLU KOROZIJAS PROCESA INHIBĒŠANĀ DZESĒŠANAS SISTĒMĀS

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Introduction

An internationally established approach to reduce corrosion attack in industrial water and in cooling systems is through the use of inhibitors. They are organic and inorganic substances that added in small concentrations into media dramatically decrease the corrosion of steel and non-ferrous metals. The boron-coordinated compounds with polyols, in particular, their sodium salts, are corrosion inhibitors of steel and non-ferrous metals in neutral aqueous and cooling solutions. In the coordination compounds boron atom is tetracoordinated and as it is known the compounds of tetracoodinated boron are not toxic, the ligands are also not toxic. Some hexols and pentols, as sorbitol, xylitol, mannitol are food products or remedies as calcium gluconate were widely studied in the Institute of Inorganic Chemistry of the Riga Technical University [1-6]. The efficiency of inhibition depends on the nature of polyol, on the content of the complex, its stability, pH of the solution, and on dimer decomposition into monomeric species, which depends on the concentration of solution. Therefore it is important to investigate the complex formation in the systems polyol– sodium monoborate–water and polyol–boric acid–water in a wide range of pH and concentrations, to foresee, which of coordination compound must be synthesized as corrosion inhibitor and what components may be added to the solution or mixed to the coordination compound to increase the inhibitory efficiency of the composition. Based on the results of chemical analysis, thermoanalytical curves, IR absorption spectra and measurements of the electric conductivity of aqueous solutions of the resulting product prove the individuality and chemical formula of sodium sorbitolborate $Na[C_6H_{14}BO_8]$. We provide the use of sodium sorbitolborate as a corrosion inhibitor in combination with additives for steel and non-ferrous metals (aluminium, copper, brass, solder) in a water-ethylene glycol mixture at volume ratio (1:1). We investigated the corrosion within the temperature range of 20-70 ^{0}C and under the dynamic conditions. coordination compounds with polyols. Polyols do not contain carboxylic groups, but contain only hydroxyl groups and their boron coordination compounds are expected to be soluble in ethylene glycol too.

Experimental

Sodium sorbitolborate $Na[C_6H_{14}BO_8]$ with the molar ratio of components 1:1 was synthesized from D-sorbitol and sodium monoborate in an aqueous solution at an increased temperature, according to the formula: $C_6H_{14}O_6 + Na[B(OH)_4]\cdot 2H2O \rightarrow Na[C_6H_{14}BO_8] + 4H_2O$.

$Na[C_6H_{14}BO_8]$ was also produced as a concentrated uncoloured transparent syrup (the concentration is 40%). Glassy sodium sorbitolborate can be obtained from the syrup by drying at 60-80 °C. The density of the concentrate at 18 °C is 1.234 g/cm^2, the boron content is 1.69%. The glassy compound may be slightly rubbed to a white powder, which is easy soluble in water and in ethylene or propylene glycols. The goal product is identified by chemical analysis: obtained in % C 30.2, H 5.38, B 4.26, Na 9.79; calculated in %: C 29.08, H 5.69, B 4.36, Na 9.27. A method to detect boron in corrosion inhibitory systems has been developed using the standard alkalimetric titration [3].
Thermoanalytical curves were taken by a derivatograph Q-1500 with heating at 10^0 C/min.
IR absorption spectra were taken by a spectrometer SPECORD as tablets (pills) with KBr.
The effectiveness of used inhibitors to reduce corrosion was expessed as percentage inhibitor efficiency calculated from the following equation: inhibitor efficiency E%= $(K_{free} - K_{inh})/ K_{free}.100$, where K_{free} and nK_{inh} are the weight losses of specimens in uninhibited and inhibited solutions respectively. The corrosion experiments were carried out at dynamic conditions at 70^0C. Duration of experiments was 336 hours and the size of metal specimens are 40.0x20.0 mm. The steel 08PC (% by weight: C 0.07, Si <0.003, Mn 0.27, S 0.020, N <0.2), aluminium (% by weight: Cu 3.8, Mg 1.2, Mn 0.3, Ni≤0.2, Fe ≤0.5, Si ≤0.5, Zn ≤0.5), copper M1, brass L63, solder 70Pb-30Sn. Samples were prepared according to the method International Standard ISO 8407, Corrosion of metals and alloys [7]. For each experiment minimum 5 samples were used. Distilled water and ethylene glycol mixture 1:1 were used as corrosion media and specimens of metals are totally immersed in the test solution. The metal specimen arrangement in corrosion cell as follow: copper, solder, brass, steel, aluminuim and the average weight loss is determined for each metal. After corrosion test corrosion products removed using a standard procedure [6,7]. Sodium sorbitolborate and additives reduce the corrosion rate of copper and brass. The synthesized sodium sorbitolborate is an effective inhibitor of the corrosion of steel, brass and copper. Among the compositions developed on its base, compositions A and D are the most appropriate.
Sodium sorbitolborate is ineffective for solder. All proposed mixtures of sodium sorbitolborate with other additives significantly inhibit the corrosion of solder. Sodium sorbitolborate does not protect aluminium – the corrosion rate even increases in the presence of sodium sorbitolborate, therefore, there is a need to use sodium-sorbitolborate-based compositions. The best results for aluminium were obtained with mixtures containing silicates of alkali metals (composition A). The protection degree reaches 85%.

Results and discussion

The thermoanalytical curves (Fig.1) of $Na[C_6H_{14}BO_8]$ under study were taken to find the main steps of their degradation.

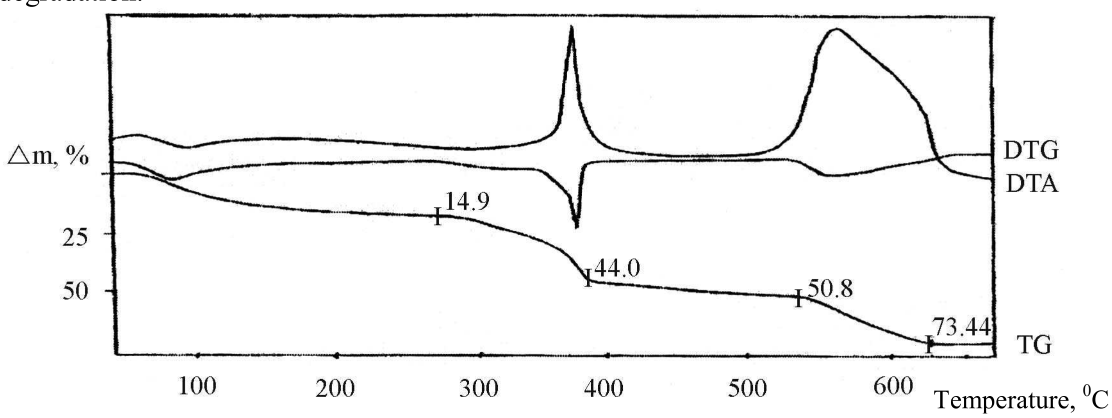

Fig.1. Termogravimetric curves of sodium sorbitolborate

Thermal decompositions of sodium sorbitolborate molecules with heating rate at 10^0 C proceed in three steps: the first one for the temperature till 280^0 C corresponding to the loss of two water molecules and weight losses are 14,90% (calculated 14,53%).The endothermal (DTG) and exothermal

(DTA) at 380^0 C (second step) is related to liberation of six coordination water molecules and weight losses are 44,0% (calculated 43,56%). The third step at 530^0 C is a complete degradation of the organic phase, and lose one molecule of water, ensuring sodium monoborate. The weight losses from the thermogravimetric curve at 630°C are 50,80% (calculated 50,85%) the residue after heating is 26.47% and identified as $NaBO_2$. The calculated from the equation weight losses and residue are 73.44% and 26.56%, respectively.

The infrared spectrum (Fig.2) of sodium sorbitolborate showed the existence of an absorption band at 950 and 1090 cm^{-1} typical of the tetra-coordinated boron atom. An absorption band at 1450 cm^{-1} corresponds to deformation vibrations, but an absorption band at 2900-2920 cm^{-1} shows valence variations of the CH_2 group. Another band in the range of 3400 cm^{-1} corresponds to vibrations of the hydrogen bonds.

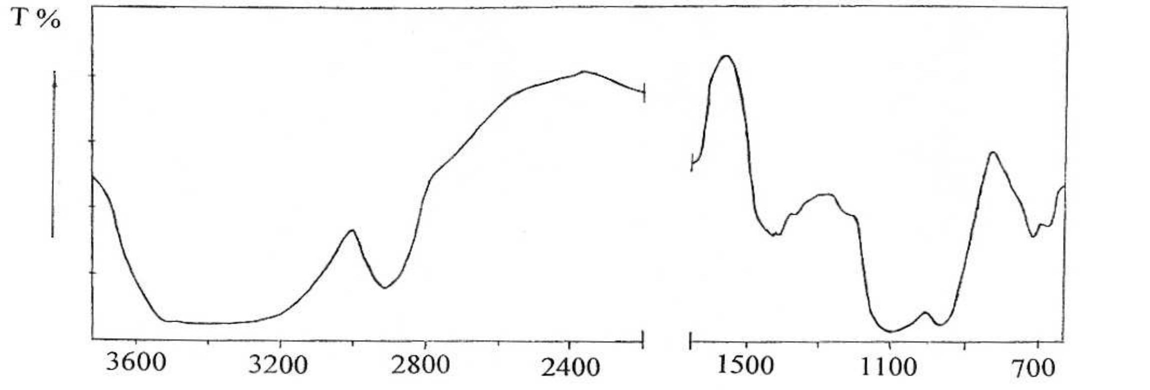

Fig. 2. Infrared absorbtion spectrum of sodium sorbitolborate

We have studied in detail the interaction of D-sorbitol with sodium monoborate by the method of isomolar series using conductometry and polarimetry. Deviations from additivity of the specific electric conductivity (Fig.3) and the rotation angle of light polarization plane (Fig.4) were investigated for the total concentrations 0.25, 0.5 and 1.0 mol/l.

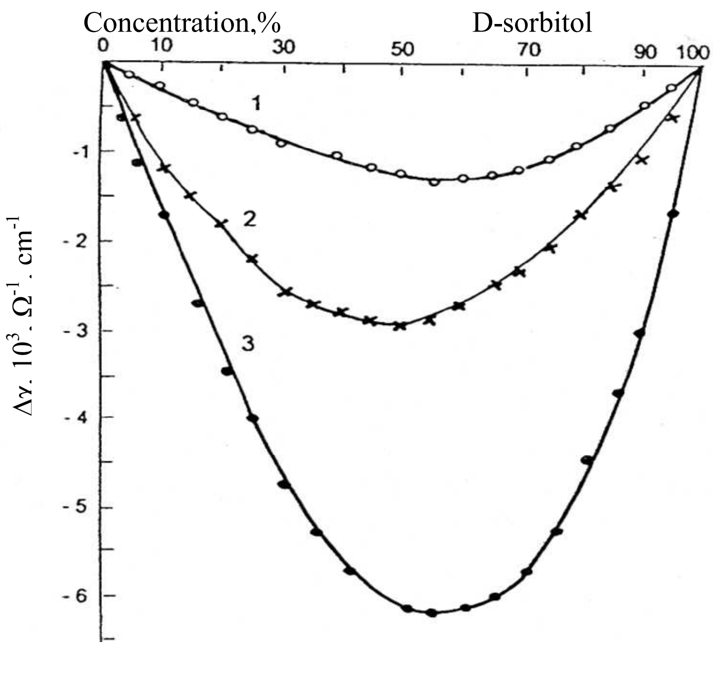

Fig.3 Deviation from additivity of specific electroconducitivity in isomolar series sorbitol- sodium monoborate-water at total concentration 1- 0.25 M; 2-0.5 M; 3-1.0 M

The decrease of the specific electric conductivity is maximum with the molar ratio of D-sorbitol to sodium monoborate being 1:1 and depends on the total concentration of the solution. When the concentration is reduced (0.25 mol/l), the maximum shifts to the right. The most obvious data are obtained from the variations of the rotation angle, which show the formation of three complex anions: $[BSorbitol_2]^-$ in acid, $[BSorbitol]^-$ and $[B_2Sorbitol]^{2-}$ in neutral and alkali zones of the system. Based on the experimental results, the concentration constants of complex anion stability were calculated $lg(K_1K_2K_3) = 5.82$.

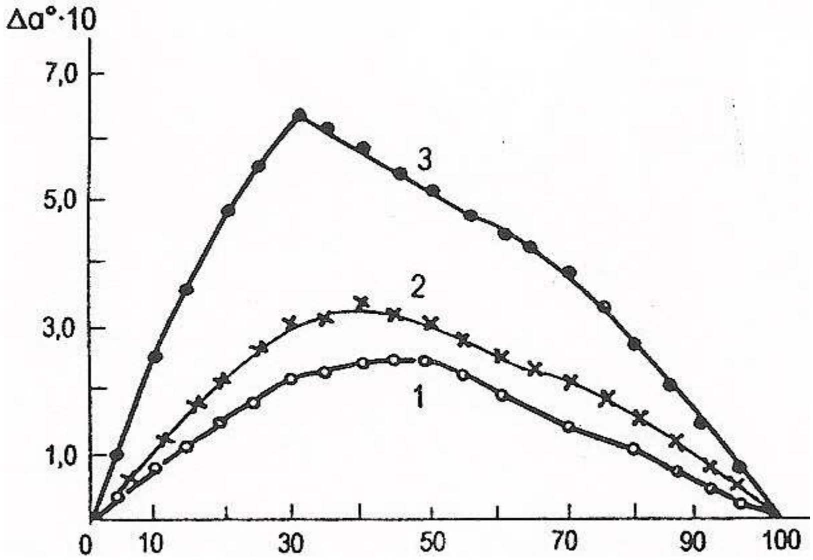

Fig.4. Deviation from additivity of rotation angle in isomolar series sorbitol-sodium monoborate-water at total concentration 1- 0.25 M; 2- 0.5 M; 3- 1.0M

Sodium sorbitolborate and sodium disorbitolborate were tested as corrosion inhibitors for steel and non-ferrous metals [8]. In the current paper, the results of the sodium sorbitolborate tests are reported.
Fig.5 illustrates the compositions (concentration, g/l) and results of corrosion tests.
Composition A-sodium sorbitol borate + Na_2SiO_3 (1,0 + 0,2 SiO_2)
Composition B-sodium sorbitol borate + N (alkali metal salt) (1 + 2,5)
Composition C- sodium sorbitolborate + Na_2SiO_3+borax + sodium benzoate (1,0 + 0,2 SiO_2 + 5,0 + 5,0)
Somposition D-sodium sorbitolborate + Na_2SiO_3 +borax +N (alkali metal salt) +sodium benzoate (1,0 + 0,2 SiO_2 +3 + 2,5 + 5,0)
For steel (Fig.5.1), in the presence of sodium sorbitolborate, an abrupt inhibition of corrosion is observed already at the concentration of 0.5 g/l, which becomes stronger with the increase of the concentration of the inhibitor, and at the concentration of 2.5 g/l the
protection degree reaches 98%. Therefore, sodium sorbitolborate itself is effective at all investigated concentrations and can be used in ethylene glycol mixtures to prevent corrosion. Since sodium sorbitolborate itself is effective, its combinations with other additives increase the corrosion rate for steel insignificantly.
The data in Fig.5.2 evidence that sodium sorbitolborate does not protect aluminium – the corrosion rate even increases in the presence of sodium sorbitolborate, therefore, there is a need to use sodium sorbitolborate-based compositions. Various mixtures have been developed – A, B, C, D. The best results for aluminium were obtained with mixtures containing silicates of alkali metals (composition A). With the ratio of sodium sorbitolborate to sodium silicate being 5:1 (in mass and recalculated for SiO_2), the protection degree reaches 85%.

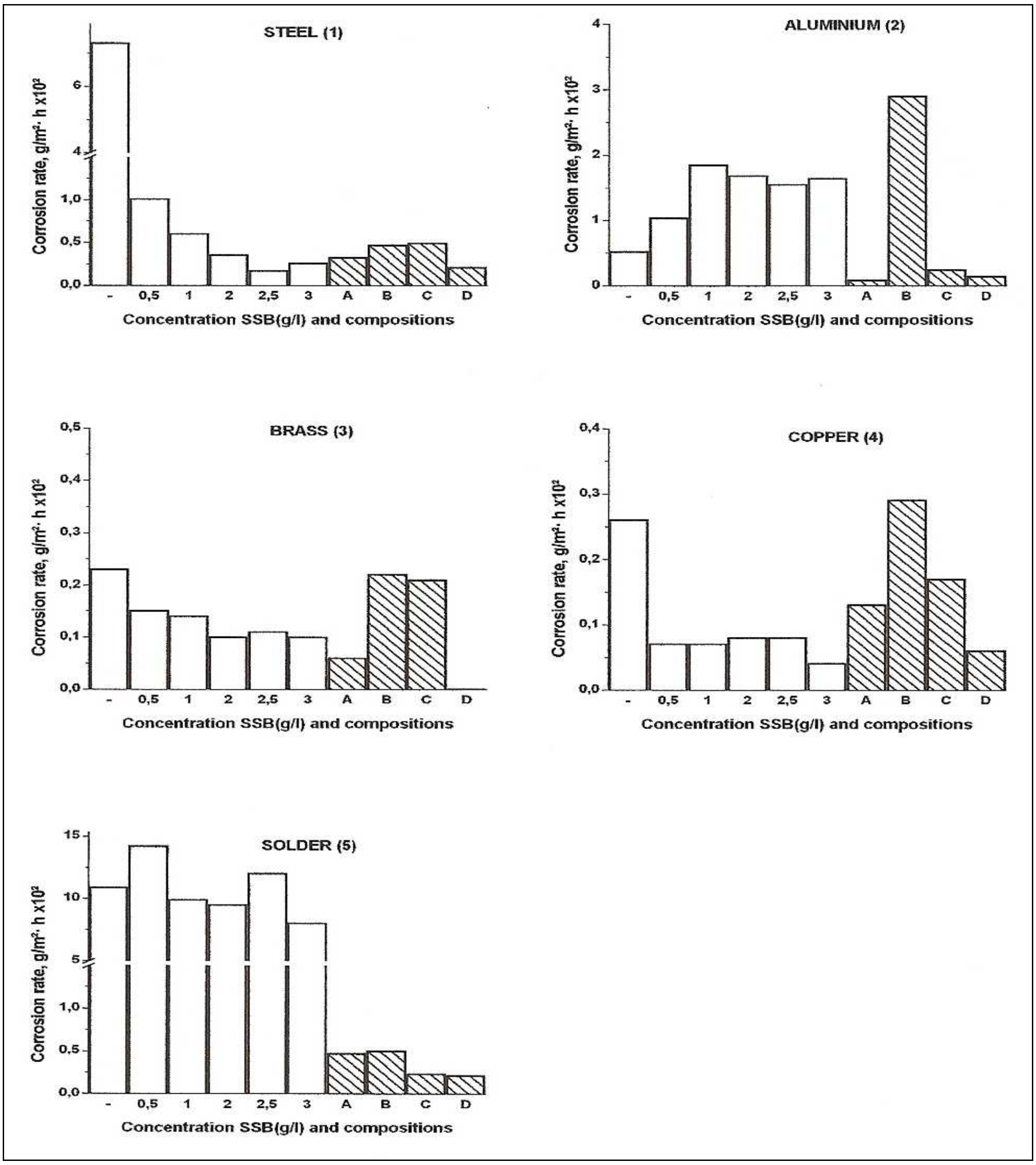

Fig.5. Corrosion of steel and non-ferrous metals. Medium ethylene glycol –water (1:1)

The corrosion rate for copper and brass (Fig.5.3 and 5.4) in the mixture of ethylene glycol and water is insignificant even without inhibitors. But, since all corrosion tests were performed in the simultaneous presence of steel, copper, brass, aluminium and solder, the corrosive influence of sodium sorbitolborate and compositions on its base was investigated for copper and brass as well. For the investigated range of concentrations, the presence of sodium sorbitolborate slows down (inhibits) the corrosion rate in 1.5-2 times. The best results have been obtained with composition D – in this case, the protection degree is 99%.

For copper, a stable inhibition starts already at the concentration of sodium sorbitolborate of 0.5 g/l and keeps constant until the concentration of 2.5 g/l (Fig.5.4). With the concentration of the inhibitor being 3.0 g/l, the corrosion rate decreases in 6.5 times. The best result for copper has been found for composition D, which almost completely protects copper against corrosion.

Sodium sorbitolborate is ineffective for solder (see Fig.5.5). At some concentrations of the inhibitor (0.5 and 2.5 g/l), the corrosion rate increases then. All proposed mixtures of sodium sorbitolborate

with other additives significantly inhibit the corrosion of solder. For examples, compositions C and D by 98% protect against the corrosion of solder, and composition A and B by 96%.
So it can be concluded that the synthesized sodium sorbitolborate is an effective inhibitor of the corrosion of steel, brass, copper. Among the compositions developed on its base, compositions A and D are the most appropriate.

Conclusions

The rotation angle and specific electroconductivity measurements have shown the formation of three complex anions. Sodium sorbitolborate and sorbitoldiborate - $[BSorbitol]^-$ and $[B_2\ Sorbitol]^{2-}$ - in neutral and alkali zones of the system were tested as corrosion inhibitors in ethylene glycol-water media.
With reference to the corrosion gravimetric measurements, sodium sorbitolborate is an excellent inhibitor for steel, and its combination with other additives influences insignificantly the corrosion rate.
Sodium sorbitolborate and additives reduce the corrosion rate of copper and brass. The synthesized sodium sorbitolborate is an effective inhibitor of the corrosion of steel, brass and copper. Among the compositions developed on its base, compositions A (sodium sorbitol borate, Na_2SiO_3) and D (sodium sorbitolborate, Na_2SiO_3, borax, N (alkali metal salt), sodium benzoate are the most appropriate.
Sodium sorbitolborate is ineffective for solder. All proposed mixtures of sodium sorbitolborate with other additives significantly inhibit the corrosion of solder.
Sodium sorbitolborate does not protect aluminium – the corrosion rate even increases in the presence of sodium sorbitolborate, therefore, there is a need to use sodium-sorbitolborate-based compositions. The best results for aluminium were obtained with mixtures containing silicates of alkali metals (composition A, (sodium sorbitol borate, Na_2SiO_3). The protection degree reaches 85%.

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Zarina I., Ignash R., Berge B. Inhibition efficiencies of sodium sorbitolborate on the corrosion of steel and non-ferrous metals in cooling media.
Rotation angle and specific electroconductivity measurements have shown the formation of three complex anions. Sodium sorbitolborate and sorbitoldiborate - $[BSorbitol]^-$ and $[B_2\ Sorbitol]^{2-}$- in neutral and alkali zones of the system were tested as corrosion inhibitors in ethylene glycol-water media. With reference to the

corrosion gravimetric measurements, sodium sorbitolborate is an excellent inhibitor for steel, and its combination with other additives influences insignificantly the corrosion rate. Sodium sorbitolborate and additives reduce the corrosion rate of copper and brass. The synthesized sodium sorbitolborate is an effective inhibitor of the corrosion of steel, brass and copper. Avmong the compositions developed on its base, compositions A and D are the most appropriate. Sodium sorbitolborate is ineffective for solder. All proposed mixtures of sodium sorbitolborate with other additives significantly inhibit the corrosion of solder. Sodium sorbitolborate does not protect aluminium – the corrosion rate even increases in the presence of sodium sorbitolborate, therefore, there is a need to use sodium-sorbitolborate-based compositions. The best results for aluminium were obtained with mixtures containing silicates of alkali metals (composition A). The protection degree reaches 85%.

Zariņa I., Ignaša R., Berģe B. Nātrija sorbitolborāta pielietošana tērauda un krāsaino metālu korozijas procesa inhibēšanā dzesēšanas sistēmās.
Ķīmiskās, termoanalītiskās analīzes dati, IS rpektri, elektrovadāmības pētījumi pierāda, ka ūdens šķīdumos eksistē trīs kompleksie anjoni. Na sorbitolbotāts un sorbitoldiborāts – $[BSorbitol]^-$ un $[B_2Sorbitol^{2-}$ neitālā un bāziskā vidē pārbaudīti kā korozijas inhibitori etilēnglikola-ūdens vidē (1:1). Korozijas gravimetriskie pētījumi pierāda, ka Na sotbitolborāts tērauda inhibēšanā sasniedz teicamus rezultātus. Sintezētais Na sorbitolborāts ir efektīvs korozijas inhibitors tērauda ,vara un misiņa aizsardzībai. Uz Na sorbitolborāta bāzes izveidotās inhibitoru kompozīcijas A un D nodrošina efektīvu lodalvas un alumīnija aizsardzību. Aisardzības efektivitāte sasniedz 85% nodrošina.

Зариня И., Игнаш Р., Берге Б. Применение сорбитолбората натрия для ингибирование коррозии стали и цветных металлов в охлаждающих жидкостях.
Измерения угла вращения и удельной электропроводности указали на формирование трех комплексных анионов. Сорбитоборат и сорбитодиборат натрия - $[BSorbitol]^-$ и $[B_2Sorbitol]^{2-}$ - были испытаны в качестве ингибиторов коррозии в нейтральных и щелочных системах. Данные коррозионных гравиметрических испытаний показали, что сорбитоборат натрия является очень хорошим ингибитором для стали.Сочетание сорбитобората натрия с другими добавками уменьшает скорость коррозии меди и латуни. Между композициями на базе сорбитобората натрия наилучшими оказались композиции A и D. Сорбитоборат натрия неэффективен для латуни, но его композиции с добавками сильно ингибируют коррозию латуни. Композиции необходимы также для ингибирования алюминия. Наилучшие результаты для алюминия получены при композиции сорбитобората натрия с силикатами щелочно земельных металлов. Степень защиты достигает 85%.