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THE ROLE OF INHIBITORS IN THE PROCESS OF FORMING A PROTECTIVE ANTI-CORROSION FILM ON THE STEEL SURFACE OF EQUIPMENT IN HEAT SUPPLY SYSTEMS

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ABSTRACT

Known methods of combating internal corrosion of metal pipes in heat supply systems, by conducting anticorrosive water treatment, cannot maximize the effect of their corrosion protection. There is no universal method of anticorrosive water treatment, each method has its advantages and disadvantages, taking into account the condition of the pipes, the speed of the water supply, and the composition of the water. However, optimal inhibition of corrosion occurring on the inner surface of pipelines of heat supply equipment can be achieved by creating a protective film on the metal inner surface of the pipe using inhibitors. Corrosion products may interfere with the good adhesion of the resulting film to the surface. For more complete and effective inhibition of the surface and dosing of the inhibitor, preliminary chemically active cleaning of the surface with a solution of sulfuric acid, at its concentration of 3%, provided for washing solutions in a circulating mode for 3-5 hours, can contribute. The metal surface of the pipe cleaned by activation contributes to a stronger adhesion of the inhibitor to the surface and the creation of a film with high protective properties. To establish the quality of the obtained anticorrosive films, a JSM-6490LV scanning electron microscope with INSAenergy dispersion microanalysis and HKL – Basic structural analysis systems with a useful magnification of 300.000 in combination with a high-performance Varian ProStar liquid chromatograph, an atomic adsorption spectrometer contrAA-300 with a plasma analyzer from 180 to 900 nm was used.The work is devoted to the selection of phosphate and high-modulus silicate inhibitors in order to form a protective film on the metal surface of the pipe to prevent the formation of scale deposits and protect against corrosion when the coolant passes through the pipe to the consumer.

Keywords: Inhibitors, Anticorrosive Protection, Effective Film, Corrosion Rate Indicator.
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INTRODUCTION

During the operation of metal equipment in heat supply systems, corrosion-scale deposits form on the inner surface of pipes, complicating the process of heat transfer to the consumer and causing the destruction of metal equipment. The internal corrosion of heating system equipment largely depends on the composition of the coolant and its aggressiveness caused by the use of water from various intakes and changing its properties even over time. There are quite a lot of ways to solve problems related to corrosion damage of metal equipment during its operation in heat supply systems. Therefore, only timely, scientifically justified methods of corrosion control will be able to ensure the standard service life of heating networks and maintain extremely normal operating modes of heat supply systems. Based on the theoretical patterns of corrosion processes occurring on the metal surface of the equipment, it is possible to develop effective means of combating corrosion damage and justify the most economically and technically feasible protection measures. One of these numerous measures is the use of various stabilizers, surfactants, and inhibitors that promote the formation of protective films on the metal surface, preventing the course of corrosion processes with possible destruction of metal equipment.The works of the authors [1-4] describe the processes of corrosion of the inner surface of metal water pipes, determined by the

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corrosive activity of the coolant (water) and the peculiarities of its operation mode, as well as methods of anticorrosive protection of metal equipment, recommendations for the use of new protection methods, including using environmentally friendly inhibitors.The improvement of the conditions for the protection of carbonaceous materials from parking corrosion of boilers based on inhibitors was shown in their works by the authors[5,6]using the inhibitor adsorption mechanism under conditions of protective film formation. By measuring the capacitance of the double electric layer, polarography, and gravimetry, the effect of the octadecylamine inhibitor (ODA) on the formation of a protective film was evaluated, and the danger of contamination of the sulfide layer was assessed.The practice of anticorrosive protection of steel equipment with inhibitors based on complexes of N-derivatives of synthetic oxy-and petroleum acids is shown in works.[7,8]In environments with hydrogen sulfide corrosion, the authors paid great attention to the selection of organic surfactants as inhibitors. By establishing a connection between the structure of an organic compound, the composition of the molecule, the length, and branching of radicals, the position and number of multiple bonds in the molecule of compounds such as resorcinol, hydroquinone, pyrogallol, ortho-, meta-cresol, the authors showed the effectiveness of their inhibitory action and adsorption on the surface of steel.[9]It is known that the main ways to combat corrosion are the use as inhibitors of some nitrogen-containing derivatives of naphthenic acids, such as imidosalines, pyridine derivatives, aliphatic amines and their derivatives, and quaternary ammonium compounds. The authors in their research have shown the development of a criterion for the protective effectiveness of the proposed inhibitor.[10-12]In various corrosive environments, corrosion destroys objects in various ways. Thus, the corrosive environment in the oil and gas industry, in the presence of such aggressive gases as sulfuric anhydride, hydrogen sulfide, and chlorine causes destruction characteristic of this corrosive environment. For this reason, it is very difficult to select inhibitors that can protect equipment from corrosion in such an aggressive environment. In their research, using gravimetric methods, the authors established the multifunctional effect of inhibitors by combining them with other compounds, for example, gossypol resin dissolved in kerosene. During the tests, a significant decrease in corrosion of steel equipment was observed with a change in the concentration of inhibitor components.[13]It is known that the main factors determining the thermodynamic possibility of the corrosion process are: the rate of the electrochemical reaction and the mechanism of its occurrence; the rate of diffusion processes that facilitate the delivery of reagents to the surface of the corroding metal, and, possibly, the removal of corrosion products. In the presence of OH-, Cl-, SO_4^{2-},and other ions in the corrosive environment, competition may arise for their more energetically advantageous place on the metal surface. If in this case, an inhibitor appears in the corrosive environment, then it is also able to participate in this competition, taking its place on the metal surface and simultaneously protecting the surface from corrosion destruction with a protective film.[14,15]To protect oilfield equipment from acid corrosion, the authors used nucleophilic compounds additionally with aminotriazole or its derivatives as inhibitors. Halides, rhodanides, and alkali metal sulfides were used as inhibitors in a mixture with urotropin or thiourea. The positive effect of mixed formulations has been shown.[16]The authors summarized and analyzed the current state of research in the field of corrosion and inhibitory protection. Experimental studies have shown the role of electrochemical, and physico-chemical research methods on the state of the issue in the field of metal corrosion, taking into account thermodynamics and kinetics. Studies have shown the effectiveness of inhibitors capable of chemisorption interaction with the metal surface and forming polymolecular protective layers of molecules chemically bonded to each other to protect metals with organic molecules.[17]The speed of water flow in the heat supply system is of great importance for the creation of protective properties of films on the inner surface of a metal pipe. In still water, soft films loosely bonded to the metal surface are formed. The authors found that it is advisable to build up films at a water flow rate of at least 0.6 m/sec. An improvement in the film quality can also be observed at higher water flow rates up to 1.2 m/sec.[18]The purpose of the study is to select a new, previously unexplored composition of mixed inhibitors, in order to create a protective film with a selected composition of inhibitors with high efficiency in protecting the metal surface of pipelines in heat supply systems.

EXPERIMENTAL

The methodology of the study on the effect of inhibitors on the formation of a protective film is outlined briefly, clearly, clearly.The following inhibitors were studied: thiourea, citric and sulfamic acids, polyphosphates, tripolyphosphates, nitrites, zinc-containing compounds, urotropin, chromates, sodium silicates with different modulus (m=1,2,3), surfactants, as well as combinations of these inhibitors.The films were built up on the metal surface of the steel samples in a special capsule device (Fig.-1), where the test steel sample was placed. Using hoses, the device was connected to a system with a capacity of 10 liters and a pump (Fig.-2) operating in a circulating mode.

Fig.-1: Capsule for a Steel Sample

Fig.-2: Installation Diagram for Obtaining Films on the Surface of a Steel Sample

To carry out the circulation process, water was poured into the container, with an inhibitor of a given composition and concentration dissolved in it. The speed of water movement in the system was regulated by a pump. The film deposition process on metal samples was carried out for a strictly defined set time.The quality indicators of the films obtained on the surface of metal samples from solutions containing various inhibitors and their combinations were established with a scanning electron microscope of the JSM-6_{490}LV brand with INSAEnergu energy dispersive microanalysis and HKL – Basic structural analysis systems with a useful magnification of 300.000 in combination with a high-performance VarianProStar liquid chromatograph (Fig.-3).

Fig.-3: Scanning Electron Microscope for Energy Dispersive Qualitative Microanalysis

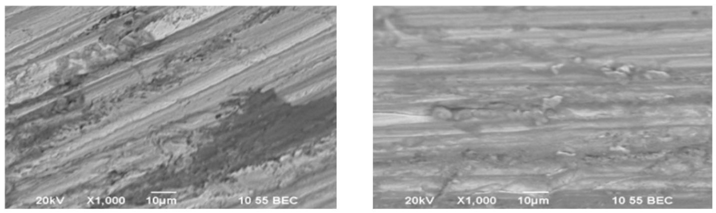
The measured corrosion rates on the metal surfaces of samples unprotected and protected by an inhibitor film were calculated for comparison by mass corrosion rates.[19]

$$K_{mass} = (\Delta m / S\cdot\tau)\ g/m^2\cdot day \qquad (1)$$

The aim of the study is to establish the role of individual and mixed inhibitors capable of forming a protective film on the surface of steel equipment to protect it from corrosion in heat supply systems.

RESULTS AND DISCUSSION

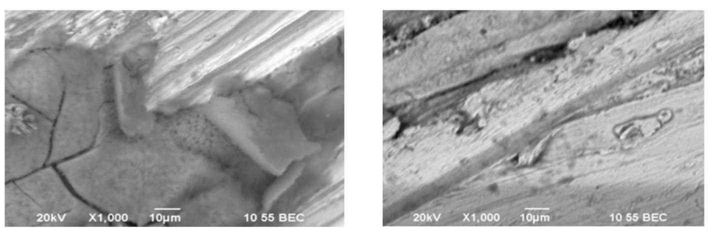
Figure-4 shows the quality indicators of films on the surface of steel samples obtained by using sodium tripolyphosphate as an inhibitor at its concentration in a solution of 3000 mg/l (No. 1) and sodium nitrite 3000 mg/l (No. 2) for 5 hours at 1000 magnification.



No.1 No.2

Fig.-4: Film Quality Indicators on the Surface of Steel Samples with Inhibitor Tripolyphosphate (No. 1) and Sodium Nitrite (No. 2)

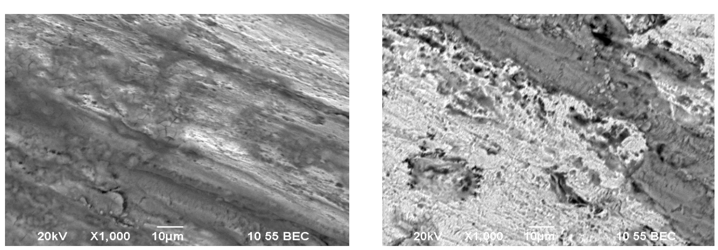
As you can see from the figure, tripolyphosphate (No. 1) forms film fragments on individual sections of the steel sample, whereas sodium nitrite forms blurred film fragments over the entire surface of the steel sample (№2).Figure-5 shows the film quality indicators:No. 3 inhibitor sodium silicate in its solution of 3000 mg/l;No. 4 thiourea inhibitor 3000 mg/l. In both cases, in 5 days at 1000th magnification.



No. 3 No. 4

Fig.-5: Film Quality Indicators on the Surface of Steel Samples with Inhibitors

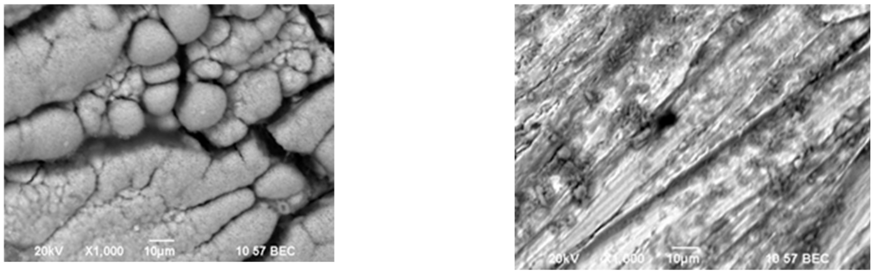
As the figure shows, the film on the surface of the steel sample is practically non-porous No. 3, which is not observed with film No. 4. Where only fragments of the film are visible in certain sections of the steel sample.Figure-6 shows a picture of a film on the surface of a steel sample with an inhibitor sulfamic acid of different concentrations in a solution of 300 mg/l (No. 1) and 150 mg/l (No. 2) at a 1000-fold magnification.



No.1 No. 2

Fig.-6: Film Quality Indicators on the Surface of Steel Samples with Sulfamic Acid Inhibitor of Different Concentrations

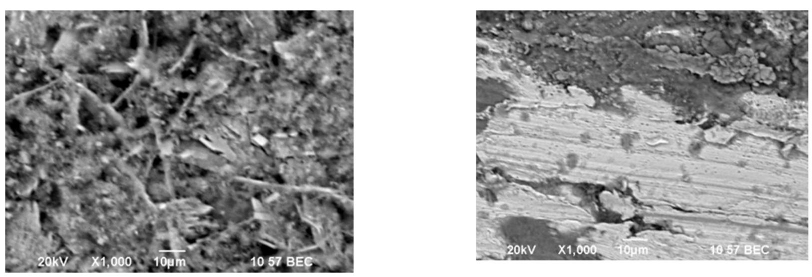
As you can see from the figure, sulfamic acid forms a dark continuous film at a concentration of 300 mg/l (No. 1), and film fragments in certain sections of the steel sample form at a concentration of 150 mg/l (No. 2).No 5 Sulfamic acid (300 mg/L) + zinc sulfate (60 mg/L) + sodium phosphate (350 mg/L);No 6 tripolyphosphate natria (250 mg/) + sulfate zinc (70 mg/l) + silicate natria (250 mg/l).The process was carried out without the use of the circulation of the solution with an inhibitor, i.e. at rest.



No. 5 No. 6

Fig.-7: Film Quality Indicators on the Surface of Steel Samples with Mixed Inhibitors

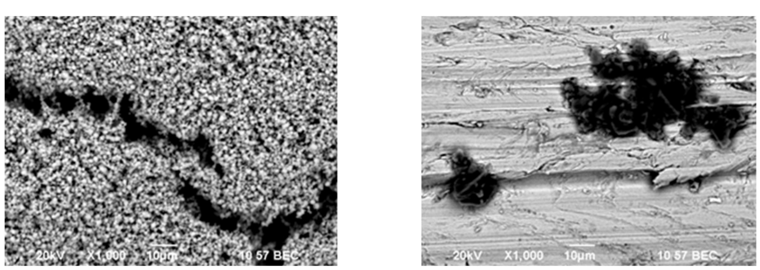
As can be seen from the figure, the mixture of inhibitor No. 5 forms a film with patches, light, with breaks. The mixture of inhibitor No. 6 promotes the formation of a solid, slightly porous film. Figure-8 shows the quality indicators of a film on a metal surface with mixed inhibitors at 1000th magnification for 5 days:No.5 Sulfamic acid (300 mg/L) + zinc sulfate (60 mg/L) + sodium phosphate (350 mg/L);No.6 Sodium tripolyphosphate (250 mg/) + zinc sulfate (70 mg/l) + sodium silicate (250 mg/l).The process was carried out using the circulation of a solution with an inhibitor, at a circulation rate of 1.2 m/sec.



No. 5 No. 6

Fig.-8: Film Quality Indicators on the Surface

As you can see from the figure, the circulation of the solution, using the same mixture of inhibitors in the solution, has a different effect on the formation of the protective film. The drawings show the best quality of the resulting films. Figure-9 shows the film quality indicators using a mixture of inhibitors:No.7 Sodium hexametaphosphate (100 mg/L) + zinc sulfate (50 mg/L) + Sodium chloride (2500 mg/L) + Calcium chloride(50 mg/L);No.8 sodium hexametaphosphate (100 mg/l) + zinc sulfate (50 mg/L) + sodium chloride (2500 mg/L) + calcium chloride (50 mg/L).The process was carried out:using the circulation of the solution at a circulation rate of 1.8 m/sec (No. 7);without circulation of the solution with inhibitors (No. 8).



No. 7 No. 8

Fig.-9: Film Quality Indicators for Surface-Grained Samples with Mixed Inhibitors

As you can see from the Figure, the mixture of inhibitor No.7 forms a fine-grained film (No.7), and a solid light film (No.8).The elemental composition and quality of the film in Fig.-10 are shown with a useful magnification of 300 000.

Element	Weight %
C	3.87
O	39.45
Si	2.48
P	16.89
S	0.46
Na	0.30
Fe	28.37
Zn	8.18
Results	100.0

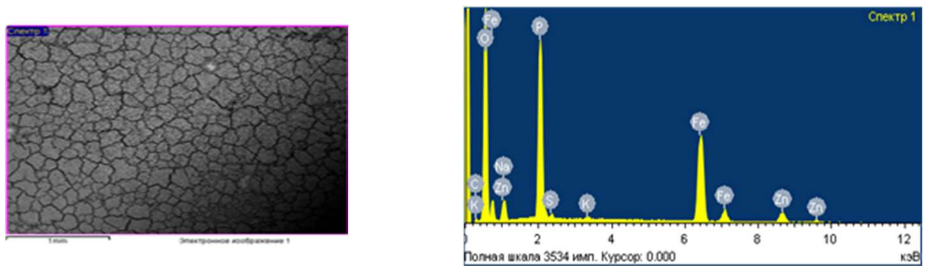


Fig.-10: Film Quality and Elemental Composition Indicators

The elemental composition of the film shown in Fig.-10 was obtained using a mixture of inhibitors: Sodium tripolyphosphate (500 mg/) + zinc sulfate (150 mg/l) + sodium silicate (2000 mg/l) with a solution circulation of 1.4 m/sec, for 10 days.When analyzing the elements in the composition of the film, a significant number of such components as silicon, phosphorus, and zinc are noted in the composition of the film. The film is light grey solid.Figure-11 shows the elemental composition and quality of the film with a useful magnification of 300.000 from a solution with the composition of inhibitors:sodium hexametaphosphate (1000 mg/l) + zinc sulfate (80 mg/l) + sodium chloride (1500 mg/l) + calcium chloride (150 mg/l), when circulating the solution at a rate of 1.4 m/sec, for 10 days.

Element	Weight %
C	3.21
O	42.02
Na	7,38
Si	3.94
P	9.54
Ca	2.09
Fe	24,92
Zn	6,9
Results	100.00

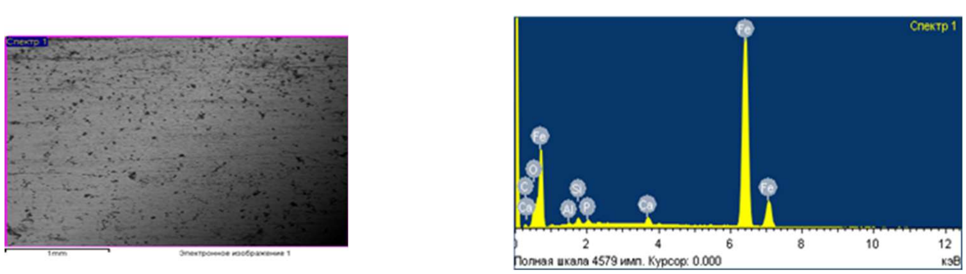


Fig.-11: Film Quality and Elemental Composition Indicators

The good quality of the film is noted – continuity, non-porosity, and lightness. The elemental composition of the film shows the inclusion of inhibitor components in the composition of the film.The analysis of the obtained data showed the advantage of the solution circulation process for obtaining high-quality films using mixed inhibitors, as well as the duration of the film formation process.To confirm the ability of the films formed on the surface of metal equipment to protect the surface from corrosion, we conducted an experiment to calculate the rate of corrosion occurring on an unprotected and protected metal surface of a metal sample.To do this, a sample of a metal pipe with a surface of 0.002 m^2, unprotected by a film, was placed in water for one, five, or ten days, after weighing the samples. At the end of the experiment, the samples were re-weighed to obtain mass (Δm).The mass index of the corrosion rate was calculated using the formula. The calculation data is shown below.

$$K_{mass} = (\Delta m / S\cdot\tau) = (3.8\times10^{-6}/0.002\times1) = 0.019\ g/m^2\cdot day \quad (2)$$
$$K_{mass} = (\Delta m / S\cdot\tau) = (4.1\times10^{-4}/0.002\times5) = 0.041\ g/m^2\cdot day \quad (3)$$
$$K_{mass} = (\Delta m / S\cdot\tau) = (2.5\times10^{-3}/0.002\times10) = 0.125\ g/m^2\cdot day \quad (4)$$

Calculations show that a longer residence time of the sample in water contributes to an increase in the rate of corrosion.A sample of a metal pipe pre-coated with a film of mixed inhibitors (sodium tripolyphosphate (500 mg/) + zinc sulfate (150 mg / l) + sodium silicate (2000 mg / l), with a circulation of 1.4 m / sec solution for 10 days, they were placed in water for one, five, ten days, after weighing the samples, as in the previous experiment. At the end of the experiment, the samples were weighed again, the mass (Δm) was determined, and the mass index of the corrosion rate was calculated. The calculation data is given below.

$$K_{mass} = (\Delta m / S\cdot\tau) = (1.02\times10^{-5}/0.002\times1) = 0.0051\ g/m^2\cdot day \quad (5)$$
$$K_{mass} = (\Delta m / S\cdot\tau) = (1.2\times10^{-4}/0.002\times5) = 0.006\ g/m^2\cdot day \quad (6)$$
$$K_{mass} = (\Delta m / S\cdot\tau) = (1.21\times10^{-4}/0.002\times10) = 0.00605\ g/m^2\cdot day \quad (7)$$

Calculations show that the corrosion rate on a metal surface protected by a film of a mixed inhibitor composition is an order of magnitude lower (0.0051-0.006 $g/m^2\cdot day$) compared with the corrosion rate on the unprotected metal surface of the sample (0.01-0.12 $g/m^2\cdot day$). It should be particularly noted that the corrosion rate of the sample on a metal surface with a protective film formed from a solution with a mixed inhibitor practically does not change (0.006 $g/m^2\cdot day$). Therefore, it is possible to make an assumption about the high protective properties of the resulting film.

RESULTS AND DISCUSSION

Based on the established quality indicators of the protective film obtained as a result of an experiment on the surface of a metal sample, in order to protect against corrosion of a metal pipe, an effective effect on the process of forming a protective film with a mixed composition of inhibitors is shown. The mechanism of formation of such a film can be represented in such a way that when ionization of iron on the surface of a metal sample in water and the possibility of formation of divalent iron compounds, the components of the mixed inhibitor also tend to take place on the surface of the metal sample, actively clinging to the surface and forming compounds of the type - ferrosilicates and ferrophosphates. The formed ferrosilicates and ferrophosphates are adsorbed on the metal surface of the sample to form a ferrosilicate phosphate film, which acquires a protective effect against corrosion.The protective characteristics of the film are also confirmed by calculations of the corrosion rate indicator. The effect of protecting a metal sample from corrosion by a film made of a mixed inhibitor is calculated and presented.Based on the results of the conducted research, we assume that the significance of the results obtained will be taken into account when selecting various compositions and mixtures of inhibitors to create a protective film on metal surfaces of equipment to prevent corrosion and free passage of the coolant to the consumer.

CONCLUSION

Inhibitors, both separate and mixed, forming a protective film on a metal surface have been studied.The compositions of the mixed inhibitors forming an effective protective film on the metal surface have been established. The protective effect of the film made of a mixed inhibitor against corrosion over a long period of exposure to the environment has been established. The efficiency of the circulation process during the formation of films on the surface of a metal sample is shown. The elemental compositions of the films were determined by a scanning electron microscope

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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