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NEW ANTI-CORROSION SOLUTIONS AND PROTECTION OF STEEL EQUIPMENT IN THE OIL AND GAS INDUSTRY AGAINST POLYTHIONIC ACID CORROSION

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Abstract

The article examines the types of new anti-corrosion solutions as a detergent for cleaning heat exchangers, evaporators and condensers from the surface of oil and gas industry facilities and the process of corrosion development with polythionic acid, as well as its effect on various stages in the oil refining process. Attention is paid to the susceptibility of nickel-based stainless steels to corrosion by polythionic acid and a modern approach to this problem is presented.

Keywords: *hydrochloric acid, hydrofluoric acid, thionic acid, desulfurization, hydrosulfuration*

Raw steel is the most widely used type of metal in the world due to its lack of complex structure and low cost as an acceptable material in modern manufacturing plants. At the same time, interest in its use is limited due to low corrosion resistance, especially in acidic and alkaline environments. The use of corrosion inhibitors is being studied by various researchers as a means of reducing the rate of corrosion and thereby reducing losses in large industrial plants and equipment. Today, inhibitors from Russian and German manufacturers are mainly imported into our republic, and the demand for them is high in water supply networks, the chemical, petrochemical, and gas industries, especially in electrochemistry.

Corrosion inhibitors usually absorb onto the metal surface and form a protective film. Research into corrosion protection methods is mainly carried out in the following areas:

- impact on metal;
- impact on the environment;
- development of combined and complex methods of protection.

This article examines a solution consisting of a mixture of hydrochloric acid, hydrofluoric acid, chelating agents, surfactants, copper complex and acridine. The solution is effective for cleaning equipment without causing corrosion. Orange inhibitor blocks anodic and cathodic areas on steel surfaces of process equipment.

Equipment used in power plants, chemical and petrochemical plants, pipelines, air conditioning units in oil refineries, and many other industrial environments are susceptible to corrosion due to exposure to chemicals released from industrial processes. Precipitated solids reduce heat transfer efficiency and often cause pipes to fail due to overheating, resulting in clogged or dirty equipment. Waterborne deposits are usually inorganic in nature, especially in hot and closed systems such as steam generators or heat exchangers. Common deposits found include sulfides, alkaline earth carbonates, sulfates and silicates.

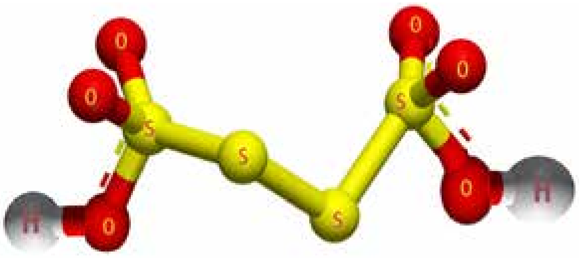
Polythionic acids are unstable and are known only in aqueous solutions. Salts of polythionic acids – polythionates – are more stable; some of them are obtained in the form of crystals. Hydrochloric acid is widely used for chemical cleaning of structural steels used in heat transfer and piping systems and produces soluble products that serve to dissolve calcium or magnesium carbonates. However, hydrochloric acid does not dissolve sulfates and silicates. Therefore, other chemicals must be mixed or added with hydrochloric acid. It is also well known that hydrochloric acid is very corrosive.

In addition, if copper salts are present in the environment, they dissolve and precipitate on iron surfaces, leading to severe local corrosion.

The purpose of this invention is to provide a non-toxic industrial cleaning composition effective for removing oxides from the surface of equipment used in various industries.

Thionic acids are characterized by sulfonic acid groups ($–SO_2OH$), which are linked directly or through sulfur atoms. The sulfur atoms in thionic acid compounds are bonded only to another S, which distinguishes them from other sulfur-containing compounds. As a special type of thionic acid, polythionic acid has a unique molecular structure characterized by many sulfur atoms.

Picture 1. *General structural formula of the thione*



In the process of gradual hydrolytic decomposition, thiosulfuric acid is thus partially converted into polythionic acids of a higher degree of sulfurization, hexathionic and, possibly, other higher polythionic acids. In the solution, along with tetrathionic acid, pentathionic and hexathionic acids were present, and in some cases higher degrees of sulfurization were revealed, since the thiosulfuric acid in the solution was partially consumed for the sulfurization of the already formed pentathionic acid. We have recently been able to prove that octathionic acid is present in the solutions obtained as a result of this reaction. But its amount in such solutions is very small; the sulfurization of hexathionic acid, i.e., the interaction of sulfur atoms in the process of increasing the length of polymer chains, occurs in a non-directional manner.

The production of a polythionic acid can be influenced by several factors, including (a) the type, concentration, and purity of sulfur-containing compounds used in the synthesis of the polythionic acid, and (b) reaction conditions such as temperature, pH, and reaction time. Sulfur-containing compounds play a decisive role in the production of polythionic acids, since they can affect the properties, reactivity and quality of the final product. The various sulfur-containing compounds used in the production of polythionic acids can significantly affect the quality of the resulting polymer, including its concentration, stability and corrosivity. For example, H_2S is a highly reactive and corrosive compound that readily reacts with oxygen and water to form a highly reactive and corrosive acid solution. Polythionic acid can also be synthesized using SO_2. However, due to the lower corrosive activity of SO_2 compared to H_2S, the resulting solutions of polythionic acid exhibit low reactivity. In addition, the initial ratio of SO_2 and H_2S can significantly affect the nature of the reaction products. When the environment is saturated with H_2S, the reaction produces elemental sulfur and short-chain polythionates, primarily S_4O_2-6.

On the other hand, when SO_2 is the main reactant, the longer chain polythionates from × 4 to 8 are mainly formed. Strong oxidizing agents such as hydrogen peroxide or elemental chlorine convert polythionates into sulfate ions (SO_2 –4). This is consistent with the fact that polythionates can degrade rapidly in the presence of small anions due to the cleavage of internal S–S bonds.

Polythionic acid can be synthesized by reacting H_2S and sulfur dioxide (SO_2) in an aqueous solution. This reaction occurs under normal conditions, including ambient pressure, temperature and a pH range of 3 to 2. When H_2S oxidizes in the liquid phase, it forms polythionate ions (S_xO_2-6). The ratio of H_2S and SO_2 in the reactants has a strong influence on the type and distribution of products formed. With an excess of H_2S, short-chain polythionates are predominantly formed, mainly S_4O_2-6. Conversely, when SO_2 is the dominant reactant, the main products are longer chain polythionates with x values between 4 and 8. The pH value of the reaction medium also plays an important role. Higher pH values lead to the formation of shorter polythionates and finally, at pH>8, thiosulfate (S_2O_2-3) is formed:

$$(2_x–5)\ H_2 + (x + 5)\ SO_2 \rightarrow$$
$$3S_xO_6^{2-} + 6H^+ + (2_x – 8)\ H_2O$$

Types of polythionic acids:

$H_2S_3O_6$ – Triton
$H_2S_4O_6$ – Tetraton
$H_2S_5O_6$ – Pentaton
$H_2S_6O_6$ – Hexatone

Polythionic acid is stable only in aqueous solutions and decomposes rapidly at high concentrations, releasing the elements S, SO_2 and sometimes sulfuric acid (H_2SO_4). Polythionate ions are significantly more stable than the corresponding acids; the most stable is polythionic acid, which contains less S in the chain (x = 3, 4, 5, 6). Among them, the least stable is $H_2S_3O_6$ – (triton). The free acid form of polythionic acid dissolves slowly in aqueous solutions, even at room temperature, forming S and sulfates (SO_2-4) as end products. Free acid exists only in the form of an aqueous solution without color or odor. In contrast, $H_2S_4O_6$ is the most stable of the polythionic acids, exhibiting properties similar to $H_2S_2O_6$ in terms of heat of dilute sodium hydroxide neutralization and electrical conductivity. The acids $H_2S_5O_6$ and $H_2S_6O_6$ are relatively stable in acidic solutions, but decompose in almost neutral or alkaline solutions to form elemental S and lower polythionates (S_4O_2-6 for pentathionic acid and S_5O_2-6 for $H_2S_6O_6$).

Temperature is critical in the synthesis of polythions and affects the reaction rate and product stability. To ensure efficient conversion of starting materials into polythionic acids, the temperature must be carefully controlled, typically within an appropriate range of 20 °C to 30 °C. At the same time, the thermal instability of the compound at extremely high temperatures (e.g. H_2S SO_2) causes the molecular bonds in the polythionic acid to become increasingly unstable and weak, leading to destruction of the chemical structure and consequent thermal degradation of the product. Reaction time significantly affects the synthesis of polythionates. Typically, longer reaction times provide sufficient time for the sulfur-containing compounds to be completely converted to polythionate. Adequate reaction time minimizes the presence of unreacted compounds and other impurities. This also helps prevent side effects or product failure.

In the refinery, polythionic acid formation is typically observed in corrosive environments with sulfur-containing compounds such as H_2S and SO_2, especially O_2 and H2O, at high temperature and low pH. Installations such as distillation columns, amine systems and sour water treatment plants are very susceptible to polythionic acid formation due to high concentrations of sulfur compounds. Desulfurization processes used in petroleum refineries, including oxidative-extractive desulfurization (ODS), oxidative desulfurization, hydrodesulfurization, adsorption desulfurization, and biodesulfurization, also contribute to the formation of polythionates as sulfur compounds.

Inflate, rotate and change during these processes.

In refineries, polythionic acid corrosion occurs in environments containing sulfur-containing compounds such as H_2S and SO_2. Corrosion by polythionic acid occurs in several stages, including the formation of acid and polythionates, attack of metal surfaces, and acceleration of corrosion. During processing, sulfur-containing compounds react with H_2O, entering into a series of chemical reactions and forming H_2SO_4. It is then oxidized to form polythionic acid. Under the influence of oxidizing agents, polythionic acid is oxidized and converted into polythionate ions, such as SO_2-4, which are soluble in water and can be mobile in the oil refining environment.

The presence of this acid can cause localized corrosion of metal surfaces due to the action of oxide layers on metal surfaces. When carbon steel is exposed to SxO_2-6, it is immediately exposed and releases hydrogen gas and forms Fe_2^+. These iron ions react with polythionates to form a protective layer of ferrous sulfate (Fe_2SO_4) on the metal surface. This can be seen in equations 2 and 4. This protective layer acts as a barrier and protects the metal from key attacks. Thus, the longevity of carbon steel tanks and pipes depends on maintaining the protective Fe_2SO_4 layer. In cases where, along with metal corrosion, a protective layer of corrosion products is formed, the rate of corrosion is determined by the slowest stage: diffusion of the oxidizer through a layer of corrosion products (Fe_2SO_4 for carbon steel), the corrosion rate is the reaction of the corrosion itself or the corrosion products away from the metal surface and the rate of diffusion into the surrounding solution.

The rate of corrosion is ultimately determined by the slowest of these stages.

$$2O_2 + 2H_2O + S_3O_6^{2-} \rightarrow$$
$$SO_4^{2-} + 2H_2SO_4$$
$$2S_4O_6^{2-} + 6H_2O + 7O_2 \rightarrow$$
$$2SO_4^{2-} + 6H_2SO_4H_2SO_4 + Fe \rightarrow FeSO_4 + H2$$

The standard method of protecting sensitive stainless steel involves preventing or neutralizing the formation of corrosion with polythionic acid. To neutralize the rot, it is recommended to wash the equipment with a weak solution of soda (1–5%) before leaving it for air.

Equipment must be soaked for a minimum of 2 hours to ensure effective neutralization. Simply treating equipment with a baking soda solution is not sufficient to prevent polythione formation. If sediment or sediment is present, the solution should be stirred vigorously by shaking for at least 2 hours. To neutralize acids, it is necessary to take into account the formation of a Na_2CO_3 film, which can additionally neutralize acids using a soda solution. Before washing with soda water, it is recommended to evaluate the effect of alkaline substances on the catalysts. It is necessary to fill the equipment with a soda solution and re-treat the surfaces with a residual soda film.

All surfaces of the equipment should be thoroughly moistened with a soda solution and rinsed with water before washing with alkali. If sulfur-containing fuel was used to fire the stove, the outer part of the stove pipes should be thoroughly washed with a soda solution to reduce the risk of corrosion by polythionic acid. Any remaining caustic wash solutions should be drained to prevent corrosion due to evaporation of carbonates and chlorides. Dryers and humidifiers should be used to prevent the formation of liquid water. These methods are designed to prevent water vapor condensation and maintain an alkaline environment by adding ammonia (NH_3) or Na_2CO_3, which provides improved protection against polythionic acid attack. These solutions provide the basis for eliminating corrosion caused by polythionic acids in refineries. The study examines the basic properties of polythionic acid, the mechanism of corrosion, its prevention and protection methods.

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