PRODUCTION OF CORROSION INHIBITORS BASED ON NICKEL PHOSPHATE

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ABSTRACT

The article presents research on the development of a multicomponent inhibitor of the polymer type, which is an effective inhibitory protection of metals from corrosion. The technology of producing corrosion inhibitors based on nickel diphosphate is shown. A comparative evaluation of the protective properties of phosphate in relation to the metal corrosion rate is given. The high degree of protection is due to the adsorption of the inhibitor, which is due to the formation of a strong Ni-Fe - containing a complex compound, leading to the growth of a difficult-to-dissolve sheeting. The analysis of various methods of obtaining $Ni_2P_2O_7$ revealed the most suitable method - this is the method of thermal decomposition $NiNH_4PO_4$.

Keywords: corrosion inhibitors, multicomponent inhibitor of polymer type, nickel diphosphate, protection of metals from corrosion.

INTRODUCTION

The finishing technology of light industry enterprises includes the mechanical processing of textile products in combination with the processing of various mixtures based on chemicals. This allows to obtain high-quality threads, yarn, fabrics possessing good consumer properties. In this regard, textile finishing equipment should have increased corrosion resistance, meet the requirements of energy, water, dyes and textile accessories, as well as equipped with automatic controls for the control and regulation of technological processes.

The technological equipment of textile enterprises is more used in conditions that are largely determined by the physical and chemical effects of conjugated parts with the environment. The surfaces of the parts are in direct contact with gaseous and liquid aggressive media, differing in composition, temperature, speed of movement, and, consequently, corrosion activity in relation to the material of the part.

In the textile industry, metal corrosion damage exceeds 5 % of the national product, so the creation and use of corrosion inhibitors should be considered an urgent task. The solution of this problem is to protect textile equipment from corrosion [1 - 3].

The analysis of patent and scientific and technical literature showed that there are companies specializing in the use of technologies for the development and application of inhibitors. Although the production and range of inhibitors are growing year after year, their composition, production technology, and production volumes are carefully protected by foreign firms. Corrosion inhibitors are used to create persistent coatings and chemical compounds that bind oxygen or other ions that serve as additives in compositions, to create coatings in circulating water systems, in water supply networks, oil refining and petrochemical industries, in any power plant, to protect microelectronics and modern military equipment, they are introduced into fuels, oils, lubricants, building materials. At present, inhibitors produced in Russia and Germany are imported in Kazakhstan and the need for them is enormous, especially in chemical, electrochemical, petrochemical, gas, textile industries, in water supply networks and circulating waters [4 - 7].

EXPERIMENTAL

Materials and methods

As the object of the study is to consider an auxiliary equipment for processing of waste of sewing and knitting production the operation of which is carried out in conditions involving water and chemicals.

The equipment includes the following components: drive mechanism, frame with needle coating, thread feed mechanism, steam and drying mechanism, mechanism for improving the thread structure. Technological equipment dissolves parts of products (breaks) of the upper knitwear and eliminates the flighting of the thread during the wet-heat treatment of the semi-finished product.

The technological scheme of the machine for processing waste of knitwear is shown in Fig. 1. From the knitwear cloth (knitwear stall) mounted on frame 1, the thread is wound through the thread guide 2, two tension devices 3, control and cleaning device 4. Passing through chamber 5, the thread undergoes wet-heat treatment and drying, and is wound on the spool 6.

The process of wet-heat treatment allows to improve significantly the structural and mechanical properties of the reused thread [8 - 13]. However, the constant use of the wet-thermal medium on the proposed auxiliary equipment leads to corrosion of the working bodies, changing the properties of the metal further worsens its functional characteristics. Partial or complete metal failure during corrosion is accompanied by the formation of oxide films, oxide or rust on the metal surface. Depending on their degree of adhesion, various cases are observed on the metal surface. For example, rust on the surface of iron alloys forms a loose layer; the corrosion process spreads deep into the metal and can lead to the formation of through ulcers and fistulas.

In addition, corrosive fatigue and corrosion cracking are also a characteristic type of corrosive destruction. Corrosion fatigue occurs at the simultaneous exposure of cyclic tensile stresses and aggressive environment and is caused by a significant decrease in fatigue limit in specific conditions compared to the limit of fatigue of these metals in the air.

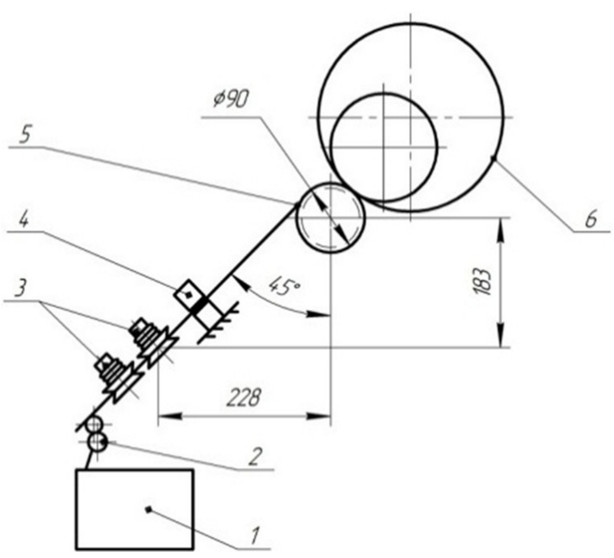

Fig. 1. Knitwear waste handling machine diagram.

Corrosion cracking occurs when the corrosive medium and external or internal tensile stresses are simultaneously exposed to the formation of transcrystalline and intergranular cracks.

Due to the presence of heterogeneity, there may be cases when the anode is a weld seam or individual areas of the thermal influence zone. At electrochemical corrosion these areas of the welded compound are dissolved, which leads to specific types of local corrosion, sometimes passing at a significant speed [14].

It is difficult to assess and predict the processes of development of local corrosion, so in many cases they lead to sudden failure of the design. In the assemblies welded structures are subjected to sufficiently rigid physical influences (aggressive environments, dynamic loads, high temperatures).These circumstances explain the high rate of destruction of welded joints and, as a result, significantly reduces the performance of the equipment, there is a large number of failures of the equipment during operation [15].

These reasons confirm the need for effective protection of metals from corrosion. To determine the effectiveness of the protection of metals from corrosion, the following methods of research are used: quantitative methods of forecasting, physicochemical methods, a method of thermal decomposition of ammonium-nickel phosphate ($NiNH_4PO_4$).

The raw materials used are:

1. Nickel (II) nitrate hexahydrate - $Ni(NO_3)_2 \cdot 6H_2O$,
2. Ammonium dihydrogen phosphate - $NH_4H_2PO_4$,
3. Activated carbon - C.

When selecting the initial substances, their physical and chemical properties were taken into account. The characteristics of the reagents used are shown in Table 1.

$Ni(NO_3)_2$ forms lightly green crystals, well soluble in water, acetonitrile, dimethylsulfoxide. It also forms crystalline hydrates of the composition $Ni(NO_3)_2 \cdot n\,H_2O$, where n = 2, 4, 6 and 9.

The most stable $Ni(NO_3)_2 \cdot 6H_2O$ crystal hydrate has a structure $[Ni(H_2O)_6](NO_3)_2$.

Water-free salt decomposes when heated:

Table 1. Characteristics of the reagents used.

Index	$NH_4H_2PO_4$	$(NH_4)_2HPO_4$	$(NH_4)_3PO_4$
T_m, °C	192,0 (with dif)	-	-
Density, g/cm^3	1,803	1,619	-
n_D^{20}	1,479	1,53	-
C°p, J/(mol·K)	142,0	182,13	230,1
ΔH°f, kJ/mol	-1445,0	-1565,7	-1671,0
Solubility in 100 g of water (25°C), g	40,0	69,5	17,7
pH 0,1 M solution	4,4	8,0	9,4
Nitrogen content, %	12,2	21,2	21,2
Content P_2O_5, %	61,8	53,8	47,6

$2\ Ni(NO_3)_2 \rightarrow$ (at 500ºC) $2\ NiO + 4NO_2 + O_2$

Crystallohydrate when heated decomposes differently:

$4\ (Ni(NO_3)_2 \cdot 6H_2O) \rightarrow$ (at 140ºC) $4\ NiO(OH) + 8NO_2 + O_2 + 22H_2O$

Ammonium phosphate is the most widely used as ammonium phosphate or ammonium polyphosphate in agriculture as a fertilizer. They contain two main nutrients - nitrogen and phosphorus in water-soluble form.

The investigation of the inhibition properties of $NiNH_4PO_4$ and $Ni_2P_2O_7$ in relation to steel samples is carried out using the standard gravimetric method. 5% sodium chloride solution is used as a model medium. The comparative evaluation of the protective properties of phosphate is determined in relation to the rate of corrosion of metal in a solution without inhibitor additives. The corrosion treatment of water by the test inhibitor is monitored by visual inspection of the surface of the steel plates and analysis of corrosion deposits.

RESULTS AND DISCUSSION

The modern classification of inhibitors includes oxidants, inhibitors of adsorption, complexing and polymeric type. This separation shows the diversity of the mechanisms of action of inhibitors and the possibility of using the achievements of various fields of chemistry to protect metals from corrosion. Corrosion inhibitors used in aquatic environments are of particular importance.

It is known that phosphates are widely used as corrosion inhibitors. In particular, various phosphates are used to prevent capes and inhibition of corrosion: Ortho-, di-, triphosphates, as well as fiberglass-like polyphosphates.

More than 5,000 steel corrosion inhibitors are now available. However, only a few groups of compounds are used, since inhibitors used for corrosion treatment of water must be harmless to humans and the environment, resistant to temperature, easily dosed, and have an economically justified cost. Widely used are the inorganic polymer phosphates.

One of the promising corrosion inhibitors are compositions, which include soluble phosphates and salts of transition metals. The most interesting are diphosphates, due to the stability of the P-O-P chain and the simplicity of obtaining. The effectiveness of inhibitors based on diphosphates from salts of 3d elements depends lightly on the composition of water. D-metal compounds increase the speed of the formation of the protective film and inhibit the corrosion of steel during its formation. However, a serious drawback of the diphosphates of 3d elements is the low rate of dissolution in water. Significantly increase the rate of dissolution of hard-to-dissolve polymeric phosphates can be achieved by the introduction of alkali metal ions or compounds capable of building into and modifying the polyphosphate chain. In particular, the solubility of nickel diphosphate can be increased by replacing part of nickel ions with NH_4^+ ions.

At the first stage of the work, an alundum crucible containing 10.54 g of $Ni(NO_3)_2\ 6H_2O$ was placed in the stove

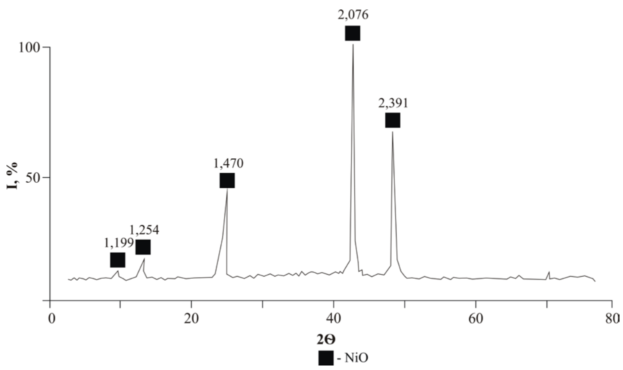

Fig. 2. The result of the NiO X-ray phase analysis.

at 400ºC for 1 hour to produce nickel oxide (NiO). The decomposition occurs according to the following reaction:

$4(Ni(NO_3)_2 \cdot 6H_2O) \rightarrow$

$\rightarrow$ (at 400ºC) $4NiO(OH) + 8NO_2 + O_2 + 22H_2O$

The obtained substance was then sent for X-ray phase analysis, Fig. 2.

In the second stage, the nickel oxide (NiO) was used to obtain $NiNH_4PO_4$. To 8.59 g nickel mass were added 18.57 g $NH_4H_2PO_4$ and 0.5 g carbon (C). This mixture was placed in a ball mill for one hour.

$2NiO(OH) + 2NH_4H_2PO_4 + C \rightarrow$

$\rightarrow$ (ball mill) $2NiNH_4PO_4 + CO + 2H_2O$

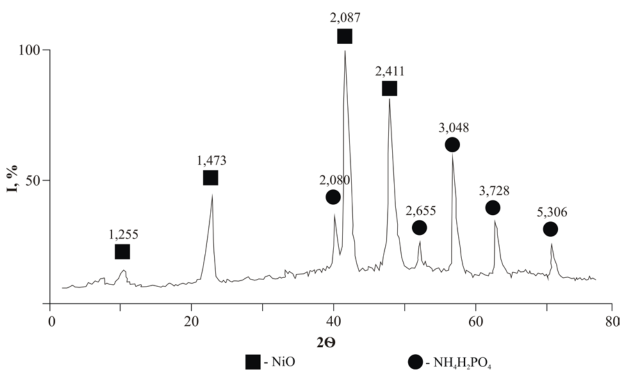

Fig. 3. The result of the $NH_4H_2PO_4$ X-ray phase analysis.

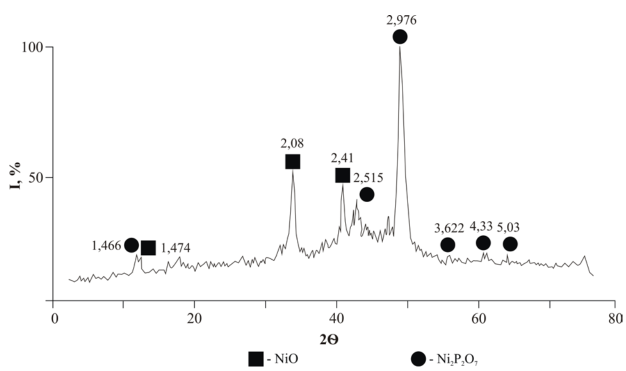

Fig. 4. The result of the $Ni_2P_2O_7$ X-ray phase analysis.

The received substance was sent for X-ray phase analysis, Fig. 3.

During the third stage, $Ni_2P_2O_7$ (nickel diphosphate) was obtained by decomposition of 12 g $NiNH_4PO_4$ in the furnace at 500ºC. The decomposition occurs according to the following reaction:

$2NiNH_4PO_4 \rightarrow$ (at 500ºC) $Ni_2P_2O_7 + 2NH_3 + H_2O$

The results of X-ray phase analysis of the received substance is shown on Fig. 4.

The output of the products is as following:

Step 1 $W_1 = \dfrac{2.73 \cdot 100}{3.45} = 80\ \%$

Step 2 $W_2 = \dfrac{14.56 \cdot 100}{16} = 91\ \%$

Step 3 $W_3 = \dfrac{6.94 \cdot 100}{8.1} = 85\ \%$

The X-ray phase analysis confirms the previously obtained theoretical data of the reaction output for obtaining NiO, $NH_4H_2PO_4$ and $Ni_2P_2O_7$.

Then the properties of the obtained inhibitors are studied. For this purpose, four steel plates are placed in four glasses containing different medium: in the first - tap water, in the second - NaCl background solution, in the third - $NiNH_4PO_4$ solution with a concentration of $1 \cdot 10^{-2}$ mol L^{-1}, in the fourth - $Ni_2P_2O_7$ solution with a concentration of $1 \cdot 10^{-2}$ mol L^{-1}. The samples are left for a week.

At the final stage, the rate constant of the hydrolysis of $NiNH_4PO_4$ and of $Ni_2P_2O_7$ at 25ºC and pH 7 are determined. The kinetic analysis of the experimental data is carried out using the equation of the first order:

$$K = \frac{2,3}{\tau} \cdot \lg \frac{a}{a-x} \qquad (1)$$

where τ - hard phase contact time with water; a - initial concentration at τ = 0, mol L^{-1}; (a-x) - final concentration at τ, mol L^{-1}.

The corrosion resistance of the steel plate in the solutions under investigation was judged by the change in the mass of the samples with the time at which the corrosion rate was calculated using eq. 2.

$$V_{corr} = \frac{(m1-m2)\cdot 1000}{S \cdot t},\ \text{mg/cm}^2\cdot\text{h} \qquad (2)$$

where: m_1 - the mass of the steel plate before experi-

Table 2. The results of gravimetric study of the inhibition ability of $NiNH_4PO_4$ and $Ni_2P_2O_7$.

No	Concentration, mol L^{-1}	Mass of the plate, g		Kav	Z, protective effect, %	γ, braking coefficient
		Before experience	After experience			
NaCl (background)						
1	NaCl	5 %	9,0534	3,1	0,06520	
			9,0403	2,9	0,05814	
			8,9843	3,2	0,06104	
$NiNH_4PO_4$						
2	$1\cdot10^{-2}$	8,7464	8,7462	2,9	98	0,02
	$1\cdot10^{-2}$	8,4473	8,4385	2,7		
	$1\cdot10^{-2}$	8,5344	8,5320	2,8		
$Ni_2P_2O_7$						
3	$1\cdot10^{-2}$	8,6225	8,6207	2,9	80,1	0,14
	$1\cdot10^{-2}$	8,9243	8,9322	3,0		
	$1\cdot10^{-2}$	8,8305	8,8298	2,9		

ence, g; m_2 - the mass of the steel plate after removal of corrosion deposits, g; S - surface area of the sample, cm^2; t - time, h.

The protective ability of Z and braking coefficient γ is calculated in accordance with the eqs. 3 and 4:

$$Z = \frac{Ko-K}{Ko} \cdot 100\% \qquad (3)$$

$$\gamma = \frac{K}{Ko} \qquad (4)$$

where: *Ko* - corrosion rate without inhibitor, *K* - corrosion rate in the presence of an inhibitor, $g/m^{-2}\cdot h^{-1}$.

Table 2 shows the changes in the mass of corrosion products formed on the surface of steel plates in the solutions under investigation, the corrosion rate, and the effectiveness of the inhibiting action Z, depending on the concentration of $NiNH_4PO_4$ and $Ni_2P_2O_7$ solutions.

From the results of gravimetric studies, it can be seen that the high protective ability of corrosion protection (98 %) shows the solution of $NiNH_4PO_4$ at a concentration of 10^{-2} mol L^{-1}, which is 18 % higher than the solution of $Ni_2P_2O_7$ at a concentration of 10^{-2} mol L^{-1}.

The high degree of protection is due to the adsorption of the inhibitor, because of the formation of a strong Ni-Fe containing a complex compound, leading to the growth of a difficult-to-dissolve sheeting.

CONCLUSIONS

Quantitative forecasting methods have shown a limited effectiveness of metal protection by individual chemical compounds, which limits the circle of previously known inhibitors. Therefore, the development of ecologically safe, low-toxic, multicomponent inhibitors becomes more urgent. Promising inhibitors of this kind are mixtures containing compounds in their composition, capable of forming self-organizing surface layers. By now, this modification of the surface of metals is a little studied area, as evidenced by the analysis of publications on the properties of polymer inhibitors.

Studies have shown that the main cause of the destruction of welded seams of textile machines is corrosion cracking under the influence of water and chemical reagents.

Theoretically and practically the properties of $NiNH_4PO_4$ and $Ni2P_2O_7$ were considered. It is established that the use of solution components on the working surface of the equipment leads to the formation of optically invisible sheeting, which are not obtained by traditional methods.

The analysis of various methods of obtaining $Ni_2P_2O_7$ revealed that $NiNH_4PO_4$ thermal decomposition method is the most suitable method.

It has been experimentally established that the obtained multicomponent polymer-type inhibitor is an effective protection of metals from corrosion.

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