ABSTRACT

«Investigation of corrosion behavior of nickel coatings in concentrated acetic acid and its vapors»

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Purpose: establish the corrosion behavior of bright nickel coatings when them are exposed to concentrated acetic acid and its vapors with the accurate determination of the effect of sulfur.

Main objectives: establish the effect of impurities of sulfur compounds on the corrosion behavior of nickel coatings in concentrated acetic acid and its vapors; determine the quantitative and qualitative composition of the surface of the coatings after exposure to acetic acid vapors; establish the mechanism of corrosion destruction of nickel coatings in the atmosphere of acetic acid vapors; develop ways to increase the corrosion resistance of shiny nickel coatings.

Object of the investigation: bright nickel coatings.

Subject of the investigation: corrosion behavior of bright nickel coatings in acetic acid and its vapors.

Nickel plating has been widely used in mechanical engineering, instrumentation, automotive and bicycle industries, production of household products and goods, to protect against corrosion of steel parts, zinc and copper alloys. Electrolytic nickel coatings are applied to the products and details to provide protective and decorative properties.

The normal electrode potential of nickel under standard conditions is 0.25 V. In air, nickel is easily covered with a thin passive film that does not change the luster and protects the metal from the destructive effects of the environment. In the case where nickel is used as a protective and decorative coating for steel, in a pair Ni - Fe can protect Fe from corrosion only in the case of non-porous coating, because nickel has a more electropositive potential.

Thin nickel coatings (1…3 μm thick) are porous. If the depolarizer penetrates the base metal, the seemingly inconspicuous pores become a center for corrosion damage. The porosity almost completely disappears when the thickness of the nickel coating is 25 ... 30 μm.

Properties of Nickel:

Characteristic	Size
Color	Silvery-white
Atomic mass	58,71
Reflective power in the visible part of the spectrum, %	58-62
Density, g/cm^3	8,9
Melting point, ºC	1452
Specific heat capacity, J/(kg·K)	0,48.103
Temperature coefficient of linear expansion, K^{-1}	12,5.10-6
Specific electrical resistance, Om· m	9,068.10-6
Electrochemical equivalent, g/(A·h)	1,095
The normal electrode potential, B	-0,25

In order to obtain non-porous protective or protective-decorative coatings use sequential deposition of several layers of the same metal or another metal of different electrolytes. In the electrochemical deposition of multilayer coatings, the pores of each layer in the coating do not coincide, so the pores overlap and the coating is less porous, which contributes to better protection against corrosion. Multilayer coatings make it possible to reduce the consumption of nickel from the electrolyte by using a cheaper metal, such as Cu.

Systems of corrosion-resistant shiny combined coatings have been developed to increase the corrosion resistance of bright nickel coatings. Those systems include coatings: bi-nickel, tri-nickel, SIL-nickel. The bi-nickel coating is characterized by a double nickel layer, in which the first layer, semi-shiny, does not contain sulfur; it is a plastic layer of columnar structure. The second layer, shiny, more brittle, contains sulfur and has a striped structure.

Bright nickel coatings are used in plumbing as a protective and decorative coating. However, there is a problem of corrosion destruction of single-layer shiny nickel coatings in domestic conditions, which are close to the tropical humid climate (high concentration of acetic acid and ammonia in bathrooms due to the decomposition of thiourea), which necessitates the application of multilayer galvanic coatings.

Nickel is a cathode coating relative to steel and can protect steel from corrosion only in the absence of pores in the coating, so in comparison with a single-layer galvanic coating is more effective coating of three-Nickel. Using this coating at each stage there is an overlap of pores and, accordingly, increases the level of protection of the metal base from the aggressive action of the corrosive environment. The peculiarity of obtaining a coating with these characteristics is due to the fact that Nickel is applied galvanically from three different electrolytes, introducing different additives.

The most common are electrolytes based on Nickel sulfate $NiSO_4.7H_2O$ because this salt is readily soluble in water up to 400 g/dm^3. Electrodeposition of Nickel is always accompanied by significant cathodic and anodic polarization, which depends on both the composition of the electrolyte and the mode of the process (in the case of passivation of the anodes, the concentration of Ni^{2+} ions in the cathode space decreases, causing a decrease in nickel current).

To prevent passivation of Nickel anodes, Cl^- ions are introduced into the electrolyte, which reduce the anodic polarization. Cl^- ions, discharging at the anode, dissolve the passive film of the anodes, thereby reducing the anodic polarization. Cl^- ions are introduced in the form of $NiCl_2$, NaCl or KCI.

To obtain a quality coating and for the correct operation of the bath should maintain a constant composition of the electrolyte. A stable pH electrolyte supports the introduction of a 3% solution of NaOH or H_2SO_4.

Matte coating are obtained from ordinary nickel plating electrolytes. After electro deposition they are polished to give them a decorative look and shine. The polishing process is very time consuming and not cheap. Also, when polishing, about 15-20% of metal is lost. For polishing you need to use expensive and scarce equipment: felt and cotton wheels, chrome mastic. To form bright platings directly in the process of electrolysis in the electrolyte are introduced special additives - shiny agents.

Nowadays, a wide variety of shinning agents are used, both inorganic and organic, but most of them can impair the physico-mechanical and anti-corrosion properties of nickel coatings, causing pitting. Conventionally, shinning agents are divided into strong and weak.

Weak shinning agents give the sediments a slight sheen and have little effect on the magnitude of the cathodic polarization of nickel. They contribute to the formation of insignificant internal stresses. Such shinning agents are, for example, saccharin and chloramine B.

Strong shinning agents (eg 1,4 - butynediol) give the sediments a significant luster and even at a small coating thickness cause a significant increase in cathodic polarization during the deposition of Nickel. Most of these shinning agents dramatically increase the internal stresses of the coating, which can cause the coating to peel off.

Shinning additives for nickel coatings are divided into two classes according to the composition of substances: organic compounds containing a group - SO_2 - (first class) and compounds containing unsaturated fragments (second class). It was also found that shiny coatings that are not inferior to mechanical and physicochemical properties can be obtained only with the use of clearly selected double and triple additives. It was found that in the presence of a benzene ring in the compound, the shining effect of organic additives is almost always effective and the coatings have a luster, with the exception of the presence of n-aminobenzenesulfamide.

It is believed that when applying a galvanic coating in the nickel precipitate includes sulfur, which gives it shine, but it is possible that sulfur change the structure and morphology of the precipitate. However, there are data on the use of organic compounds that do not contain a sulfo group. For example, it is proposed to use isonicotinic acid and 2-oxy-4,6-dimethylpyrimidine.

Many shinning agents contain sulfur in their chain, which can affect the corrosion behavior of shiny nickel coatings. From the above information it is clear that in the literature the mechanism of influence of sulfur, which is present in the shining agents, on the corrosion behavior of shiny nickel coatings is a controversial issue.

In, the influence of sulfur inclusions on the corrosion behavior of electrolytic nickel-iron alloys is considered. In this paper, it is mentioned that sulfur is included in the coating due to the introduction of shinning agents into the electrolyte, while it increases the susceptibility to corrosion and the corrosion rate of these coatings. Matulis found that during the deposition of Nickel in the presence of saccharin, two reactions occur simultaneously at the cathode: hydrogenation of saccharin without sulfur cleavage (sulfur with an organic chain) and with complete cleavage of sulfur from the molecule to form benzamide and sulfamide. These reactions take place simultaneously in the adsorption layer.

Similar studies by Butken and Mockute confirmed that during the deposition of the alloy on the content of benzamide in the mixture of saccharin degradation products is lower than in conventional nickel plating. They also noted that the resistance of the coating to corrosion depends on the method of inclusion of sulfur in the sediment.

The result of shows that even in the presence of a low concentration (0,3 g/dm^3) of saccharin in the electrolyte, the sulfur content in the coating is already 0.05%. When the saccharin content increases to 1 g/dm^3, the inclusion of sulfur is suitable and remains unchanged (about 0.1%). This may be due to the fact that the concentration of sulfur in the coating continues to increase while the corrosion rate decreases. The authors also noted that depending on the sulfur content in the coating, there is a difference in the morphological structure of the coating (smoother or rougher), which in its situation affects the rate of corrosion of the deposited coating. However, the affect of the sulfur or any mechanism of corrosion of nickel coatings for the presence of sulfur was not proposed.

Pitting corrosion – local destruction of metals in the form of individual affected areas. This process is characteristic of metals and alloys capable of passivation, such as chromium-nickel steels, nickel, aluminum and others, exploited in sea water, atmospheric conditions and soil. A type of pitting corrosion is the corrosion of multilayer systems.

It is generally accepted that the conditions leading to pitting corrosion are the presence of oxidants and aggressive anions in the solution, primarily chlorides. Energy heterogeneity of the metal surface also leads to pitting corrosion. Heterogeneous inclusions are energetically advantageous places of origin of pitting. Elimination of all or the most active inclusions leads to increased corrosion resistance of metals.

On pure metals, the origin of pitting is the defects of the crystal lattice, such as clusters of dislocations. As the number of non-metallic inclusions increases, the number of areas affected by pitting increases, which leads to a decrease in the rate of pitting corrosion in these areas.

The process of formation of pitting nuclei is possible within the passive region. The probability of formation of pitting corrosion nuclei increases with increasing potential and decreases with decreasing defect of the passive surface. Pre-thickening of surface oxides leads to inhibition of pitting. As the temperature of the corrosive medium and the concentration of activating anions increase, the influence of the initial state of the surface on the formation of the pitting decreases; activity against "weak" surface defects increases. In some cases, it is possible to merge all the formed pitting, which leads to delocalization of the dissolution process. It is believed that such a transition may be useful, as pitting corrosion turns into less dangerous uniform corrosion.

Known methods of combating pitting corrosion, which consist in increasing the degree of purity of the metal, the use of corrosion-resistant alloys, the use of corrosion inhibitors, the implementation of electrochemical protection.

The most common multilayer systems that are subject to pitting corrosion in atmospheric conditions are protective and decorative coatings (nickel - chromium, copper-nickel-chromium, etc.). The mechanism of pitting corrosion of these multilayer coatings is associated with the potential difference between chromium and nickel. It is believed that the passivated chromium is the cathode, while the lower layer of Nickel, exposed in the pores or cracks of the chromium layer, becomes the anode of the corrosion system. The large cathode surface and the small anode surface create conditions conducive to the rapid development of corrosion damage in the form of a pitting in the nickel layer.

The dissolution of nickel continues even after the corrosion damage has reached the copper layer, which also begins to dissolve. At a time when steel is already beginning to break down, the process of anodic dissolution of copper and nickel almost stops. Degradation of coatings usually occurs faster in industrial areas with polluted air containing sulfur dioxide and in the northern coastal area with a high content of aerosols of seawater salts in the air.

Increasing the protective properties of copper-nickel-chromium coatings is achieved by changing the dynamics of the corrosion process by including several nickel layers (bi-nickel, tri-nickel), which differ in electrochemical behavior.

In two-layer coatings consisting of semi-shiny (less than 0.005% sulfur) and shiny (0.05% sulfur) nickel layers, the corrosion rate of the semi-shiny layer is significantly lower than the corrosion rate of shiny. This ratio of corrosion rates contributes to the fact that the fracture is localized mainly in the layer of shiny Nickel. Corrosion fractures, reaching the boundary of the layers, continue to develop in the direction parallel to the surface of the sample, in a layer of shiny Nickel and to a much lesser extent there is the development of corrosion deep into the base metal or semi-shiny layer.

A further increase in the protective properties of the coatings is obtained due to the introduction between the semi-shiny and shiny Nickel layers of a thin layer of Nickel (2-3 μm thick) containing 0.12-0.15% sulfur. This coating is called tri-nickel. When applying three layers of Nickel, the pores overlap and, accordingly, the level of protection of the base metal from the aggressive effects of corrosive environments increases. The peculiarity of this coating is that Nickel is applied galvanically from three different electrolytes, introducing various additives.

In the dissertation are shown E-pH diagrams for systems containing Nickel and dissolved in a solution of sulfur and oxygen. These diagrams make it possible to assess the risk of corrosion, as modification of the sulfur-coated surface can significantly affect the corrosion resistance of nickel and nickel alloys.

After processing the literature data, a number of experiments were performed.

Their essence was:

a) obtaining galvanic nickel coatings of different thickness (nickel foil 50-100 microns, samples 6 microns thick);

b) conducting corrosion tests in acetic acid and its vapors (capturing of polarization curves, massometric measurements);

c) SEM-investigation of the surface of the samples after exposure to acetic acid vapor;

d) established the mechanism of corrosion of nickel coatings in concentrated acetic acid and its vapors;

e) the effect of sulfur on corrosion processes on nickel.

To solve the problem of corrosion destruction of shiny nickel coatings in acetic acid and its vapors, measures have been developed to increase corrosion resistance, which consists in the application of two-layer nickel coatings.

To verify the stability of these coatings in acetic acid vapor, studies were performed. Samples were weighed on analytical balances before and after exposure. Test samples of two-layer nickel coating were deposited in accordance with the technology specified in table 3.2. Samples precipitated from nickel plating solutions were also used separately (three samples in each electrolyte).

After 2 hours of exposure of the samples in acetic acid vapor, obvious traces of corrosion are visible only on nickel samples that were precipitated from a solution containing saccharin. Characteristic traces of green nickel corrosion products were observed on these samples. Other samples did not have such drops on the surface.

After 26 hours of exposure, all samples were noticeably destructed because of corrosion. From the results of massometric measurements it is seen that the samples with bi-nickel coating have less weight loss of the sample. This is due to the fact that in comparison with a single-layer glossy coating containing sulfur inclusions, the bi-nickel coating is more stable in acetic acid vapor. This is made possible by blocking the access of oxygen to the surface of the layer containing saccharin (the first layer of bi-nickel coating). This overlap of the lower nickel coating, in fact, prevents its dissolution and subsequent formation of galvanic pars and the corrosion rate is slowed down.

According to the methodology of the thesis, the experimental part of the research work was performed using harmful and dangerous substances and materials.

At the laboratory we worked with toxic liquids, namely acids (sulfuric, hydrochloric, acetic) and acetic acid vapors, with the electrical connection used in glassware.

All technical decisions were made taking into account the requirements of labor protection. In the dissertation was given section with analysis of dangerous and harmful factors and means for maintenance of safe working conditions, fire prevention and safety in emergency situations.

Nowadays in the chemical industry much attention is paid to automation. The presence of automated processes helps to increase productivity. In this dissertation with the help of automation succeeded:

1) reduce labor costs in working in an aggressive environment;
2) ensure compliance with a clear sequence of the technological process;
3) reduce the probability of error due to the reduction of the influence of the human factor.

Thus, the main parameters of the galvanic bath, which are associated with the establishment of an automatic line, are:

- temperature;
- acidity of the electrolyte;
- electrolyte level in the bath;
- current and voltage in the bath.

KEYWORDS: galvanic coating, nickel, Watts electrolyte, corrosion, sulfur-containing compounds, acetic acid, technological card.