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Development of chromate-free passivation processes for galvanized steel

Abstract

Relevance of the research

Zinc coatings applied by electrochemical or hot methods are widely used to protect steel products from corrosion. Zinc coatings have a high protective ability for steel and provide cathodic corrosion protection in a humid atmosphere.

Zinc coatings, due to their high electronegativity, have low corrosion resistance and are quickly destroyed in corrosive environments. Until now, the most widely used method for increasing the corrosion resistance of zinc coatings remains the process of passivation in solutions based on hexavalent chromium compounds, despite the serious disadvantage of this process - the high toxicity of the solutions used. If chromate solutions get into the environment (for example, due to accidents, leaks), the chromate ions present in them can cause significant damage. Chromate coatings themselves also contain toxic Cr(VI) compounds. For example, chromated parts of modern cars contain up to 200 mg/m^2 of hexavalent chromium.

Currently, most developed countries have adopted laws regulating the maximum permissible concentration of Cr (VI) in drinking water, reservoirs and wastewater, limiting or completely prohibiting the use of Cr (VI) compounds in mechanical engineering and electronics.

Along with their high protective ability, an advantage of conversion chromate films is their ability to self-heal, which significantly extends the service life of metal structures.

The disadvantage of chromate coatings is their low heat resistance: when heated (to temperatures of 160°C and above), their protective ability sharply decreases, which is unacceptable for parts operating, for example, in the engine compartment or other "hot spots" of cars.

Passivation in solutions based on compounds of the less toxic trivalent chromium has not found a wide practical application, since the resulting passivation

films do not meet the mechanical strength, protective ability and the self-regeneration requirements.

More promising are the relatively new IV generation chromite coating processes with consequent application of a surface protective layer from film-forming solutions with silicon nanoparticles, the so-called sealers. Chromite coatings of the IV generation like chromate films, are capable of self-regeneration and can withstand 300 hours in a salt fog chamber until the first manifestations of white corrosion. However, these processes are not yet widely used in practice due to the relative complexity of implementation and control, as well as the high cost compared to chromate plating.

Due to the tightening of environmental requirements for mechanical engineering and electronics products, the use of toxic compounds of metals such as nickel, cobalt, chromium in the manufacture of protective and decorative coatings is limited. Therefore, the development of processes for the production of conversion protective coatings on zinc that do not contain compounds of these metals is an urgent scientific and technical problem.

According to the scientific literature, a promising alternative to chromate coatings may be coatings formed in solutions containing environmentally safer compounds of rare earth metals (REM) instead of chromate ions.

The purpose of the work

The research objective is to develop a process for applying protective chromate-free conversion coatings to galvanized steel surfaces in order to replace toxic chromate plating processes and study the mechanical and physicochemical characteristics of the resulting coatings.

The research tasks:

1. Establishment of formation patterns of chromate-free conversion coatings and the influence of various factors upon their characteristics.

2. Assessment of the influence of the concentration of rare earth metal compounds in the cerium-containing solution on the protective characteristics of the resulting coatings.

3. Assessment of the influence of the concentration of sodium metasilicate in the working solution on the protective characteristics of the resulting coatings.

4. Development of a methodology for assessing the self-healing ability of conversion coatings.

5. Determination of the chemical composition of the resulting chromate-free conversion coatings.

6. Study of the protective ability and wear resistance of the resulting coatings and their comparison with the properties of iridescent chromate coatings.

7. Determining of paint adhesion to a passivated surface obtained in the developed solutions.

8. Optimization of solution compositions and regime parameters of the processes of obtaining the developed coatings.

9. Study the stability of the developed solutions and conditions for their adjustment.

Scientific novelty of the research.

1. For the first time, it was established that the introduction of lanthanum nitrate into the cerium-containing zinc passivating solution leads to an increase in the protective ability of the resulting coatings when the ratio of cerium ions to lanthanum ions in the solution is equal to 2:1, and the total concentration of REM in the solution is equaling to 3 g/l. It was shown that the increase in the protective ability occurs due to the reduction the number and the diameter of pores in the resulting coatings.

2. For the first time, it was discovered that in the process of self-healing of a cerium-lanthanum-containing coating on a galvanized surface, the proportion of Ce^{3+} compounds in the newly formed coating in damaged areas increases.

3. For the first time, hydrogen peroxide stabilizers have been determined, which not only increase the service life and stability of converting solutions, but also do not reduce the protective ability of the silicon- and cerium-lanthanum-containing coatings.

Practical significance of the research.

1. Technological processes for the application of protective silicon- and cerium-lanthanum-containing coatings onto galvanized surfaces that can replace highly toxic chromating processes have been developed. The developed coatings can be used both as independent protective coatings and as adhesive layers under paint or varnish coatings.

2. A new comprehensive method for assessing the self-healing ability of conversion coatings has been developed.

3. It has been established that the introduction of sodium pyrophosphate into the solution for the formation of passivating conversion cerium-containing coatings increases the resource and stability of the solution by 2 times, and the introduction of sodium pyrophosphate in combination with saccharin into the solution for the formation of passivating conversion silicon-containing coatings increases the service life and stability of the solution by 2,5 times.

Provisions for defense

The results are submitted for defense:

1. Dependence of the characteristics of conversion coatings on the composition of solutions and process parameters.

2. Data on the self-healing ability of the coatings, the proposed mechanism of self-healing of cerium- and cerium-lanthanum-containing coatings.

3. Results of the assessment of the functional properties of the developed passivating coatings.

4. Adjustment mode for the developed solutions for the application of passivating coatings to galvanized surfaces.