Improving zinc-rich epoxy primer performance with lamellar zinc incorporation

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Abstract

It is estimated that 25 % of the world's steel produced annually is destroyed by corrosion and, since steel is used on a large scale, corrosion can lead to high losses. Among the forms of corrosion protection for carbon steel structures exposed in different atmospheres, painting is one of the most used. Zinc rich paints are commonly used as a paint system primer for carbon steel protection exposed to highly corrosive environments. Thus, zinc rich paints have the function of protecting against corrosion and imparting adhesion to the metal substrate. This study proposes a zinc rich paint formulation in which part of the spherical metallic zinc microparticles is replaced by lamellar zinc particles, providing better packaging with lower zinc content in the film which aims at ensuring better mechanical performance of this coating. A significant increase in the mechanical properties of the developed formulation was achieved when compared to a commercial zinc rich paints without compromising its conductivity.

Keywords: corrosion, coating, lamellar zinc, mechanical property, zinc rich paint

1. Introduction

The steel is one of the most widely used alloys in the world, being produced on a large scale and at relatively low costs. Due to its properties and enormous versatility in composition and conformation, steel has been used in the production of machinery, equipment, vehicles and, above all, in civil construction. However, it is estimated that 25 % of the world's steel produced annually is destroyed by corrosion [1]. Thus, it is necessary that this material will be protected, in order to mitigate corrosive processes.

Among alternatives for anticorrosive protection for carbon steel structures exposed in different environments, painting is one of the most used [2]. Currently, several types of anticorrosive paints are available, whose chemical formulations vary according to the requirements of the applications for which they are intended [3], [4].

The so-called zinc-rich paints (ZRPs) have as their main characteristic the high concentration of spherical zinc micro-size particles in their formulation, in order to ensure that the percolation limit between the zinc particles in the film and the steel is reached. These paints

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are commonly used as primer in painting systems to protect carbon steel exposed in highly corrosive atmospheres, whose function is to protect against corrosion and to give adhesion of the painting system to the metallic substrate [5].

Due to the presence of zinc particles (Zn) in ZRPs applied to steel, cathodic protection is initially promoted, with preferential corrosion of zinc (sacrificial anode, less noble metal than iron) and a consequent protection of the metallic substrate [6]. In addition, as a consequence of the formation of zinc corrosion products around the particles over time, barrier protection occurs. This protection mechanism is due to the difficulty of penetrating aggressive agents through zinc particles covered with corrosion products which reduces the attack of the substrate [7].

However, in recent years, there has been an intensification of studies related to ZRPs, mainly in an attempt to improve their mechanical properties and it is possible to note that there is a tendency to reduce the zinc fraction of these formulations, because the high concentration of solids on the film results in lower adhesion and flexibility properties [8], [9].

Among the possible solutions to this problem, the replacement of part of the spherical zinc micro-size particles by zinc nanoparticles or other conductive nanomaterials has been studied, thus providing a better packaging with less amount of zinc in the film and, consequently, improvement of the mechanical properties. Another option often mentioned in the literature is the use of lamellar morphology particles (such as lamellar zinc and alumina), as they are able to guarantee the electrical conduction in the coating and to potentiate the barrier effect, using less amount compared to the spherical particles [10], [11].

Thus, with the partial replacement of spherical zinc micro-size particles by lamellar zinc particles in the formulation, this work aims at obtaining ZRPs with a reduced zinc concentration in relation to a conventional paint available in the market and that present better mechanical properties (flexibility and impact resistance) and better adhesion to the substrate without compromising its conductivity, thus being able to offer adequate anti-corrosion protection.

2. Methodology

2.1 Materials

A commercial zinc-rich paint (ZRP) epoxy-based, according to the approval requirements of the Brazilian standard PETROBRAS N1277:2017, was used as a reference. An amide-based hardener agent was used as component B. As a basis for preparing the modified paint, the commercial paint formulation without the addition of metallic zinc was used. Metallic zinc lamellar particles (STANDART Zinc flake GTT, ECKART Effect Pigment) were used to partially replace the metallic spherical zinc particles (MICROZIN 2500 BRASÓXIDOS, Brazil) in the modified formulation. For mechanical tests, steel substrates were used with characteristics required by specific standards of each test.

2.2 Preparation of modified ZRP with lamellar zinc particles

The base formulation of the reference was mixed with the metallic spherical zinc particles and the metallic lamellar zinc particles. The stirring was performed using a mechanical stirrer coupled to a Cowles impeller. The rotation used was 800 rpm for 20 min. A hardener agent is needed for application and this quantity is proportional to the amount of resin in the modified formulation.

2.3 Characterization of the modified and commercial ZRPs

The conductivity of modified and commercial liquid paints was measured using a conductometer with an electrode Cond probe InLab 741-ISM by Mettler Toledo.

The solid content of the dry film was measured according to ISO 3251-2008.

The sample preparation and the coating process were based on Brazilian standard PETROBRAS N1277-2017. The pull-off adhesion test was carried out according to ASTM D4541- 2017. The direct impact test, to available the adhesion, flexibility and tenacity by fast deformation, was carried out according to ISO 6272-1:2002. The bend test (conical mandrill), to evaluate the flexibility by slow deformation, was carried out according to ISO 6860:2006. The Erichsen *Cupping* test, to provide the flexibility by slow deformation and the capability of deformation after failure, was carried out according to ABNT NBR 5902-1980.

3. Results and Discussion

3.1 Characterization of the modified and commercial ZRPs

The values obtained in the characterization of commercial and modified paints are shown in **Table 1**. The formulation modified with lamellar zinc has a higher amount of resin (8.6 %) compared to the reference paint (6.8 %). However, with the partial replacement of micrometric zinc by lamellar zinc, a reduction in the solids content (89.4 %) compared to commercial paint (91.5 %) was obtained, however, the electrical conductivity of the liquid paint was not compromised, presenting values in the same order of magnitude as the reference.

Table 1 - Characteristics of liquid paint and dry film of ZRPs commercial and modified

ZRP	Liquid paint		Dry film
	Conductivity (S/cm)	**Resin fraction (%)**	**Solid's fraction (%)**
Reference ZRP	1.64×10^{-7}	6.8	91.5
Modified ZRP with lamellar zinc	2.64×10^{-7}	8.6	89.4

The comparison of the results of mechanical tests performed with the reference and modified TRZs are shown in **Figure 1**.

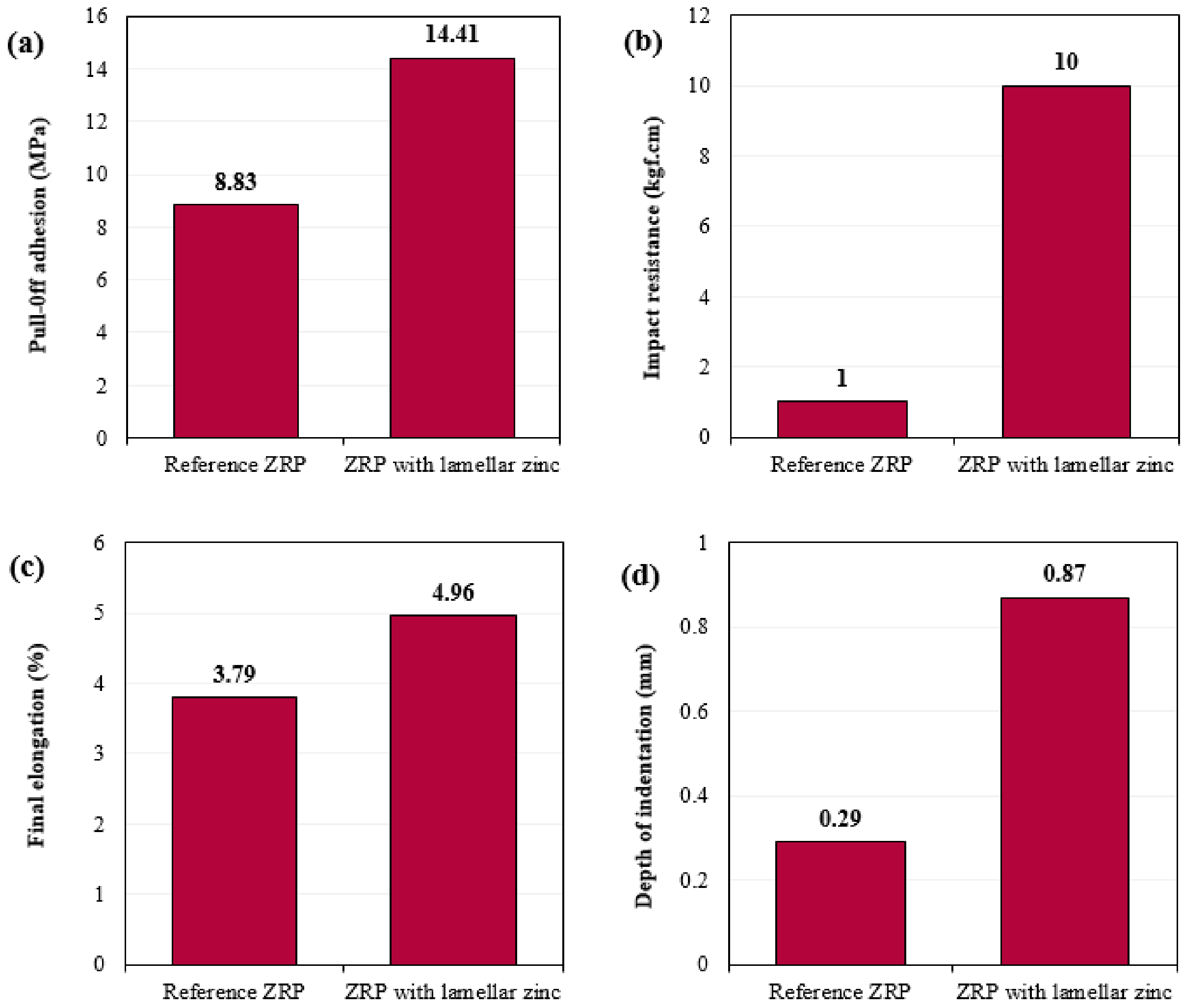

Figure 1 - Mechanical properties of reference and modified ZRP: (a) Pull-off adhesion test, (b) impact resistance, (c) conical mandrill bend test and (d) Erichsen cupping test

The modified formulation ZRP with lamellar zinc (14.41 MPa) resulted in an increase of 63.2 % in the pull-off adhesion value of the dry film in relation to the reference (8.83 MPa), as shown in **Figure 1(a)**, being observed in both paints cohesive failure (100B).

As shown in **Figure 1 (b)**, the result of the direct impact test, associated with the ability of the paint to absorb more energy during impact (rapid deformations) without fail, showed a 900 % growth in the resistance value presented by ZRP with lamellar zinc (10.0 kgf.cm) compared to the reference ZRP (1.0 kgf.cm).

The bend test (conical mandrill) result, used to evaluate the flexibility by slow deformation and the ability to undergo plastic deformation, is shown in **Figure 1(c)**. It can be seen an increase of 30.9 % in the final elongation value of the ZRP with lamellar zinc (4.96%) in relation to the result obtained by the reference ZRP (3.79 %).

Finally, considering the Erichsen cupping test in **Figure 1(d)**, there is a 200 % increase in the indentation depth with the ZRP with lamellar zinc (0.87 mm) compared to the commercial reference paint (0.29 mm). This test is related to flexibility by slow deformation of the substrate and the capability of accommodating deformation after failure.

Conclusions

According to the results observed, the decrease in fraction of solids and increase in value of resin on the dry film of ZRP promoted better mechanical properties of the coating, with a desirable increase in the adhesion, cohesion and flexibility properties of the modified paint with lamellar zinc.

For the protection mechanisms offered by the ZRPs, electrical conductivity is a fundamental factor. The conductivity measurement in liquid paint modified with lamellar zinc was comparable (same order of magnitude) to that of the reference paint which indicates that the electrical contact between the conductive particles (spheric micro-size zinc and lamellar zinc) in the film was not compromised by the new formulation. Corrosion tests are being performed to compare the protection performance of the new formulation in comparison to the reference.

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