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Valuation of mill scale as iron pigments for painting anticorrosive

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Abstract

The mill scale is a steelmaking byproduct. This work focuses on the valuation of the steel waste and its transformation to a usable product in the field of anti-corrosion paints. These iron oxides have been examined as a pigment and corrosion inhibitor in two types of paints with different concentrations (1 %, 3 %, 7 %, and 15 %) to determine the best formulation. Their properties were compared to that of an anticorrosion paint trademark based on iron oxide. For this purpose various techniques of mechanical and physical-chemical analysis were used; grinding is applied to pieces of mill scale for very fine powders (< 32 µm); the particle size of the milled scale analysis, to determine their particle size distribution; a primary electrochemical method used to evaluate the performance and scale vis-à-vis the phenomenon of corrosion behavior, and a UV-Visible spectroscopic method for determining the concentration of total dissolved iron. The experimental results showed that the anti-corrosion properties or rather inhibition efficiency increases with increasing concentration of the mill scale in the tested paints.

Keywords: mill scale, corrosion inhibitor, spectroscopic, electrochemical analysis.

1. Introduction

The mill scale, a byproduct of steelmaking process, is produced by superficial oxidation of the slabs and billets of steel during the cooling in continuous casting and during the reheating process and hot forming [1]. The treatment of the scale for reutilization basically depends on local conditions and on the main technological approach of each region or country [2]. Generally, these co-products have been the object of a considerable number of research works for the different areas: decontamination [3-6], concrete and mortar [7, 8], pigments [1, 2] and renewable energy [9].

The pigments derived from iron oxide are increasingly important due to their chemical stability, non-toxicity, durability, low cost and wide variety of colors: black, yellow, brown and red [10, 11]. It is estimated that about 85 % of metal structures, exposed to different aggressive environments, are painted [12]. For this reason the paints based on metal pigments are used as corrosion protection.

The pigments are used in all areas of daily lives: plastic, glass, paper, paint and coating [11-13].
The purpose of this work is twofold:

- From an environmental perspective: the ability to enhance the ecological issue that is reinforcing the protection of the environment.
- From an economic perspective: operating scale as metallic pigment in paints for corrosion protection.

2. Materials and methods:

2.1. Commercial materials

The following commercial components have been used for anticorrosive paint preparation (two types of solvent borne paints):

- Glylac (long oil alkyd): this is a lacquer for building.
- Glycar (medium oil alkyd): it is a lacquer for vehicle body and steel structures.

The two selected paints are marketed by the Algerian National Company of Paintings (ENAP). The protection by these paints is compared and estimated with regard to an anticorrosion paint trademark [1] with iron oxide. To emancipate the influence of uncoated substrates (control), dummy tests were conducted in parallel with the coated samples.

2.2. Mill scale preparation

The waste material used in this work is mill scale and it was obtained from The Steel Complex of El-HADJAR[2]. Table 1 reports that the chemical compositions of the mill scale sample contains predominantly of iron oxides (hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO)) with small amounts of Si, Mn, Ca oxides. Figure 1 shows the particle size distribution of mill scale sample.

Table 1:
Chemical composition (%) of the mill scale

Component	Fe_{total}	FeO	CaO	SiO_2	MnO
%	72,3	56,9	0,42	0,14	0,37

[1] *ANTI: anticorrosion paint trademark*
[2] *El-HADJAR (Annaba,600-km east of Algiers)*

2.3. Paints preparation

We have incorporated the mill scale pigment with different concentrations (1 %, 3 %, 7 %, and 15 %) for both types of paints to determine the best formulation.

Designation:

- *Glylac + 0 % mill scale pigment = LAC 0*
- *Glylac + 1 % mill scale pigment = LAC 1*
- *Glylac + 3 % mill scale pigment = LAC 3*
- *Glylac + 7 % mill scale pigment = LAC 7*
- *Glylac + 15 % mill scale pigment = LAC 15*

- *Glycar + 0 % mill scale pigment = CAR 0*
- *Glycar + 1 % mill scale pigment = CAR 1*
- *Glycar + 3 % mill scale pigment = CAR 3*
- *Glycar + 7 % mill scale pigment = CAR 7*
- *Glycar + 15 % mill scale pigment = CAR 15*

2.4. Samples preparation

The paints were applied with a brush onto steel substrates and air-dried for 24 h. The used metallic substrates are rectangular (80×50mm) steel plates of 1 mm thick. The metallic substrates have been immersed in a sodium chloride solution (NaCl) at 3.5 % for 45 days at room temperature before testing. These substrates are unscrewed into two series:

- Full immersion: for spectroscopic analysis
- Partial immersion ($12.56 cm^2$): for electrochemical measurements

2.5. Test methods

Sieve analysis performed by Laser Granulometry (Hydro 2000MU) (average of three measurements).

- A UV–visible (Jenway) spectrophotometer was used for iron analysis at 510 nm wavelength, according to the standard methods (Colorimetric O-Phenanthroline Method) [14].

- The electrochemical measurements (Tafel experiments) were carried out with an EG&G model 273A potentiostat/galvanostat (±250 mV in relation to OCP).

3. Results and Discussion

3.1. Sieve analysis

Figure 1 shows a histogram which is output from the Malvern laser particle analyzer software. Examining figure 1, we see that the grain in the 10-micron Bin, each of a series of ranges of numerical value into which data are sorted in statistical analysis, represent about 5 % of the total volume of the powder pigment. The average grain size of pigment was 6 µm and specific surface area of 1.6 m^2/g. (Dv90) where 90 % of the total volume of the pigment is made up of grains with diameters smaller than or equal to 20 µm.

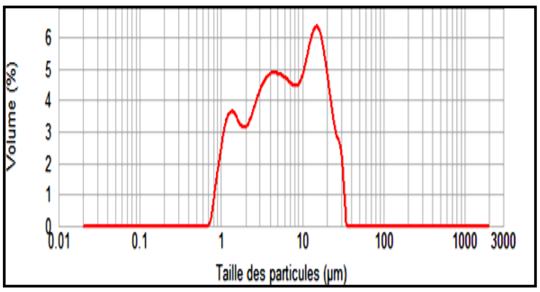

Figure 1: Particle size distribution

3.2. Electrochemical measurements

3.2.1. Corrosion potential monitoring

The evolution of the random potential during a test of corrosion is a first index to estimate the degradation during the dumping. Figures 2 and 3 show the corrosion potential versus time plot. The x-axis shows the immersion time. The y-axis gives the corrosion potential in Volts versus the Ag/AgCl/KCl electrode was used as reference electrode. The stability curve as a function of the immersion time of the metallic substrates coated with the Glylac paint at different pigment concentrations are shown in figure 2.

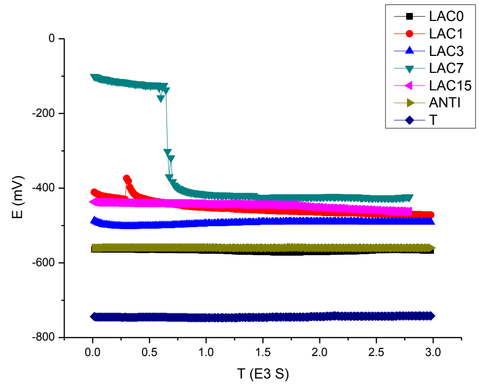

Figure 2: Corrosion potential versus time plot of the metallic substrates coated with the Glylac paint and various concentrations of mill scale pigment, in 3.5 % NaCl medium

For the Glylac paint coating (Figure 2), the potential increases with increasing mill scale pigment concentration towards more noble values to stabilize at a plateau located between –400 and –560 mV/SCE.

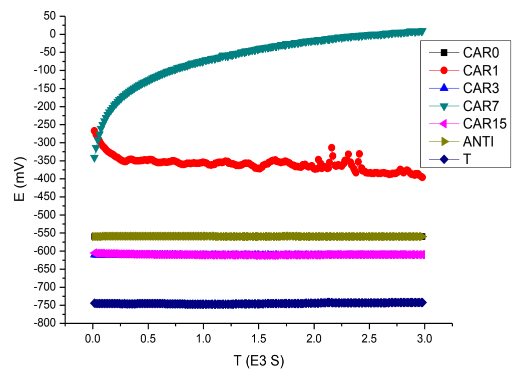

Figure 3: Corrosion potential versus time plot of the metallic substrates coated with the GlyCar paint and various concentrations of mill scale pigment, in 3.5 % NaCl medium.

For the GlyCar paint coating (Figure 3) in general may notice improvement in the inhibitory efficiency of paint if the pigment is added to the latter.

3.2.2. The polarization curves

The Potentiodynamic polarization curves for the metallic substrates (bare and coated) immersed in an aqueous NaCl solution are shown in figures 4 and 5.

Regarding the polarization curves of the Glycar paint, there is a failure for the three formulations CAR 0, 1, 7, since the coating isolates the system (no current flow between the electrodes). For this we operate the coordinates (**$E_{(I=0)}$, I_{corr}**) calculated as shown in figure 5.

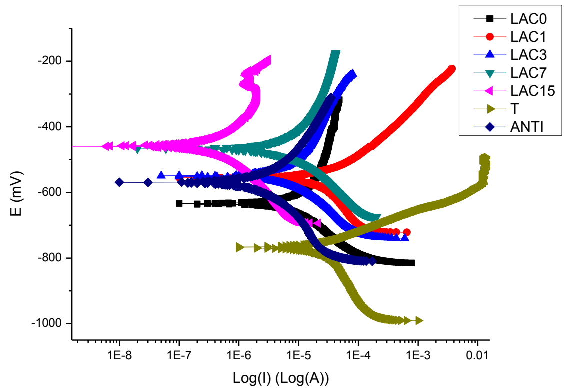

Figure 4: Potentiodynamic polarization curves for the metallic substrates coated with different formulations of Glylac paint

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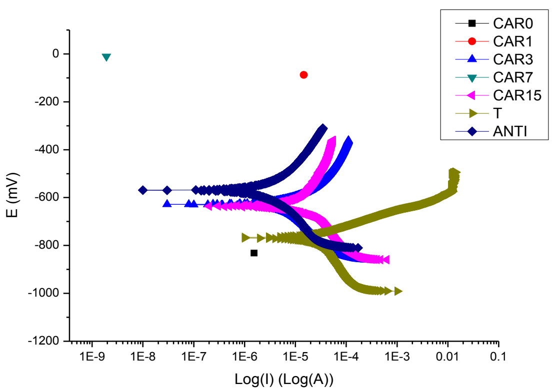

Figure 5: Potentiodynamic polarization curves for the metallic substrates coated with different formulations of GlyCar paint.

Polarization curves (Figures 4 and 5) show that the concentration of pigment affects positively the potential and the current density. It should also be noted that the formulation Lac15 moves the corrosion potential in the positive direction of about 111.1 mV / ECS compared to the anticorrosion paint trademark. Furthermore, the decrease in the corrosion current is proportional to the content introduced of pigment. The opposite would happen with different formulations of GlyCar paint (improvement is not proportional to the content introduced of pigment)

3.2.3. The UV-visible spectroscopic analysis:

The absorbance of a material in solution is directly depends on the concentration of that material, or in other words, the absorption increases with increase in the concentration of a solution [15]. The absorbance reading at wavelength of about 510 nm was used (maximum absorbance (λ_{max})). Figure 6 shows the curve of absorbance which was plotted from these readings for Spectrophotometric analyses.

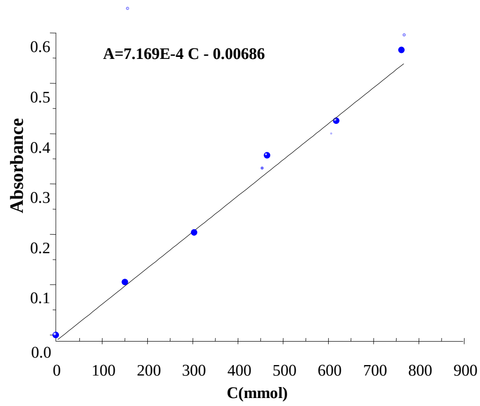

Figure 6: Calibration curve of iron ions by spectrophotometry in the presence of orthophenanthroline

Two methods allow us to determine the concentration of iron ions dissolved from the metallic substrates totally immersed:

- Either by linear interpolation of the sample absorbance at headlined the calibration curve

- Or by direct use of mathematical model previously obtained: C = (A + 0.00686) /7.169 E-4

For a better assessment of the effectiveness of pigment, we converted the iron concentration in corrosion rate (R_c), taking it to the corresponding control (bare metal) as being equal to 100 % (Figure 7.).

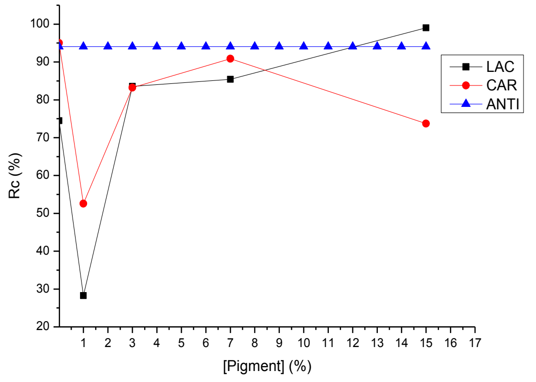

Figure 7: Corrosion rate (T_c) for different formulations

The results are used to compare the effectiveness of different formulations not only among themselves but also with respect to commercial anticorrosive paint as the reference or landmark. They show that:

- For each type of formulated paint, there is a rate optimal pigment for which protection against corrosion of the substrates is maximal.

- The corrosion rate of the substrates coated with the formulation ANTI is catastrophic. Perhaps, it was attacked by the ions that exist in a harsh environment; it is known that the system corrodes easily in similar conditions.

- There is a good agreement between the electrochemical analysis and spectroscopic analysis, with the exception of the formulation ANTI that gives an unacceptable result for the last method, because of not using the same conditions for both methods.

4. Conclusion:

In the present work, we became interested in two issues:

- Ecological issue that is reinforcing the protection of the environment.

- Economic issue; operating scale as metallic pigment in paints for corrosion protection.

The results obtained by different techniques of mechanical and physical-chemical analysis can be summarized as follows:

- Chemical analysis showed a total average iron content of 72 % and low contents of other oxides.

- Particle size analysis that shows a volumetric size distribution D (0.9) of the particles has a size less than 21 micrometer and a specific surface area of 1.6 m2 / g

- For each type of formulated paint, there is a rate optimal pigment for which protection against corrosion of the metallic substrates is maximum, 15 % for Glylac and 7 % for Glycar.

- The Glycar paint alone is more efficient than the commercial anti-corrosive paint itself in these conditions.

- The best formulations can be classified according to their inhibition performance as follows:

LAC3>LAC1>LAC7>LAC15>CAR15>
CAR0>CAR1>ANTI>LAC0>CAR3>CAR7

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