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Inhibitor properties of "green" pigments for paints

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Abstract

Zinc chromate is one of the anticorrosive pigments most frequently used in the formulation of primers. However, its environmental aggressiveness and toxicity severely restrict its use, and different green alternatives have been proposed in order to replace zinc chromate. In the last decade, the behaviour of zinc phosphate as anticorrosive pigment has been intensively researched. During this time, various modifications have been made to this family of pigments to improve its properties, and a "second generation" of phosphate pigments, incorporating elements such as molybdenum, aluminium, or iron, has been produced. In this paper, the inhibitive properties of zinc phosphate and three second-generation phosphates have been investigated, using zinc chromate pigment as a reference. Pigment extract solutions, at different values of pH, have been used as corrosive media. Carbon steel samples were immersed in such solutions and their corrosion rates were measured using electrochemical techniques. The data obtained suggest that zinc chromate provides the highest percentage of inhibition in neutral and basic solutions, but phosphate-based pigments showed better results in acid solutions. Given this performance advantage, together with their less harmful environmental impact, these phosphate-based pigments can be proposed as realistic alternatives to chromates in the formulation of protective paints for use in acidic conditions.

Keywords: Corrosion; Pigments; Inhibition; Phosphate; Carbon steel; NaCl; Extracts

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1. Introduction

Organic coatings are commonly used to protect metals and alloys against corrosion. It is estimated that approximately 85% of metal structures exposed to different corrosive media are painted [1]. World wide, paint and coatings production is a mature industry worth some $ 50 billion with a predicted future growth rate of 2–5% p.y. [2]. The different types and colours of paint available, the different application processes and possibilities for combining paints with other coatings have made it a complex decision to select the most suitable paint for specific types of corrosion protection [3].

Pigments are one of the basic components of primer formulation. Usually, inorganic crystalline solids are used as pigments [4]. Pigments in paints can play many different functions, such as supplying colour or enhancing their chemical or physical strength. Other pigments act as inhibitors increasing the resistance of metal surfaces to corrosion [5]. The inhibitor action of anticorrosive pigments takes place in different ways. Thus some inhibitor pigments act by improving the barrier properties of the coating. These kinds of pigment have a physical activity, in that they separate the metallic substrate from the corrosive medium. Other pigments show a chemical activity and can be classified in four groups according to their mechanism of action [6]. First, some pigments decrease the rate of anodic reaction by binding the metal ions produced by corrosion reactions, and as a consequence, coordination compounds are formed at anodic zones. Other pigments decrease the activity of both anodic and cathodic processes by liberating passivating ions. A third kind of pigment reacts with the resin, giving rise to compounds that decrease metal corrosion. The last kind of pigment acts by increasing the concentration of OH^- ions in water diffusing through the porous paint. In steels, this increase of pH decreases the activity of metallic corrosion processes [7].

In general, chemically active pigments are soluble substances that dissolve continuously in the water that permeates through the coating, giving rise to an inhibitive solution that reaches the coating–metal interface. Among this kind of

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pigment, those most extensively used are red lead and zinc chromate, because of their efficiency [7]. However, these compounds are highly toxic and cause serious environmental pollution [8]. Hence, in recent decades, the surface finishing industry has undergone fundamental changes in respect of the development and promotion of environmentally friendly pigments for primer formulation [3,7,9–15]. In this context, zinc phosphate has been proposed as an alternative pigment. This compound has a level of toxicity 50 times lower than chromates [8]. Further, the use of phosphates does not represent an excessive cost, and their application is even easier than other proposed alternatives [12,16].

However, the mechanism by which primers pigmented with zinc phosphate provide protection against metal corrosion is not well established. The anticorrosive behaviour of this compound has been related to the reaction between zinc phosphate and some acid resins [17–20]. This reaction produces a metallic soap that acts as an anodic inhibitor [4]. In primers that do not contain acid resins, it has been proposed that zinc phosphate dissolves in the water that permeates the paint [21], and when this solution reaches the metallic substrate both Zn^{2+} and $PO_4{}^{3-}$ ions slowly re-form as phosphate on the metallic surface. It is thus proposed that an additional passivation of the surface takes place [4,22–24].

Primers pigmented with zinc phosphate have been studied using different characterisation procedures. When accelerated tests were used, the estimated inhibition level was lower than when long outdoor exposure tests was employed. According to [10], the discrepancy between long and short tests data are due to the slow rate at which the zinc phosphate reaction takes place. However, most authors [7,10,12,21,25–27] explain these differences in terms of the low solubility of the pigment.

In order to improve the protective behaviour of these substances, a "second-generation" pigment based on zinc phosphate has been developed by adding elements such as molybdenum or aluminium [7]. Improved behaviour has been observed from primers pigmented with basic zinc molybdenum phosphate hydrate, basic aluminium zinc phosphate hydrate and basic zinc phosphate hydrate with an organic pre-treatment [7]. However, there is little information in the bibliography on such second-generation zinc phosphates.

In this paper, the anticorrosive behaviour of several commercial inhibitor pigments has been studied. The selected pigments were zinc phosphate, zinc chromate, dibasic lead phosphite and three phosphate-based second-generation pigments: zinc and aluminium phosphate, ferrous and zinc phosphate and zinc phosphomolybdate. In order to evaluate their inhibition capacity, the pigments have been extracted in 3.5% NaCl solution at different values of pH. This procedure is intended to simulate the behaviour of pigments dispersed in paints [3,21,28,29]. The extracted solutions have then been employed to evaluate the corrosion rate of a commercial carbon steel, using electrochemical techniques.

Table 1
Chemical composition of pigments

Pigment	Composition
Zinc chromate	$3ZnCrO_4 \cdot K_2CrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$
Dibasic lead phosphite	$2PbO \cdot PbHPO_3 \cdot \frac{1}{2}H_2O$
Zinc phosphate	$Zn_3(PO_4)_2 \cdot 4H_2O$
Zinc–aluminium phosphate	$xZn_3(PO_4)_2 \cdot yAlPO_4 \cdot zH_2O$
Zinc–iron phosphate	$wZn_3(PO_4)_2 \cdot xFeO(OH) \cdot yFeHPO_4 \cdot zH_2O$
Zinc phosphomolybdate	$xZn_3(PO_4)_2 \cdot yZnMoO_4 \cdot zH_2O$

2. Experimental

2.1. *Chemical composition and conditions of extraction of the pigments*

As already commented, six commercial pigments have been studied. Their chemical composition is given in Table 1.

In order to simulate the working conditions of the pigments in paints, extracts of each pigment were prepared at room temperature and different pH conditions. The extractions were carried out by shaking 500 mg of the pigment in 1 l of a 3.5% NaCl solution, for 24 h at 700 rpm. The solution was then filtered to remove the undissolved pigment. After filtering, the extracts were used as electrolyte for studying the corrosion behaviour of carbon steel.

Each pigment was extracted in three different pH conditions, giving rise to:

- *Neutral extracts*. The pigments were extracted without external modifications to the pH. In this case, the pH values measured are close to 7 for each pigment.
- *Acid extracts*. The pH of the extracts was externally modified by adding HCl to reach a value of 4.5.
- *Basic extracts*. The pH of the extracts was externally modified by adding NaOH to reach a value of 10.5.

The prepared extracts were analysed in order to determine the concentration of the dissolved species. The analysis was carried out using an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) of Philips, model PU 70000.

2.2. *Metal alloy*

Orthohedric samples of 100 mm × 75 mm × 6 mm of DIN Std. The 35.8 carbon steel were used in this study. The composition of this material is given in Table 2. Workpieces were ground with SiC paper of 80 grits and cooled under running water. They were then degreased with ethanol and rinsed with distilled water immediately prior to the tests.

2.3. *Electrochemical measurements*

After surface preparation, one sample of the carbon steel was immersed in each of the extract solutions, until a stationary state was reached. Linear polarisation (LP)

Table 2
Composition of DIN Std. 35.8 carbon steel

Elements (%)											
C	Si	P	S	Mn	Al	Cr	Mo	Ni	Co	Cu	Sn
0.126	0.188	0.017	0.009	0.667	0.028	0.023	0.001	0.009	0.011	0.020	0.008

measurements were made after 15 h of exposure of the metal samples to the electrolyte. These electrochemical tests were performed in a Solartron potentiostat/galvanostat, model SI 1287. A Crison Ag/AgCl (0.207 V vs NHE) electrode was used as reference electrode. The polarisation rate was 10 mV min^{-1}. In addition, intervals of polarisation of ±10 mV around the corrosion potential were used to estimate the polarisation resistance (R_p). The effect of each pigment was evaluated using the parameter of percentage inhibition power (%IP), calculated from the equation:

$$\%\mathrm{IP} = \frac{R_{\mathrm{Pe}} - R_\mathrm{P}^0}{R_\mathrm{P}^0} \qquad (1)$$

where %IP is the inhibition power of the evaluated pigment, R_{Pe} the polarisation resistance of carbon steel immersed in the studied extract and R_P^0 the polarisation resistance of carbon steel immersed in 3.5% NaCl solution at the corresponding pH value.

3. Results and discussion

3.1. Chemical composition of extracts

Pigment extracts were prepared following the procedure described above. Their chemical composition was analysed using ICP-AES spectroscopy to measure the concentration of the elements obtained from the pigment in each extract (Tables 3–8).

Comparing the results reported in these tables, in each case studied, the highest pigment solubility is reached in the acid pH condition. As will be shown later, these values correlate with the inhibition power of the extracts.

Table 3
Concentration of Zn and P in zinc phosphate extracts

Zinc phosphate	[Zn] (mg/l)	[P] (mg/l)
Neutral extracts	5.69	1.22
Basic extracts	<0.05	1.25
Acid extracts	111	32.7

Table 4
Concentration of Zn and Cr in zinc chromate extracts

Zinc chromate	[Zn] (mg/l)	[Cr] (mg/l)
Neutral extracts	92.0	92.4
Basic extracts	3.37	89.9
Acid extracts	168	104

Table 5
Concentration of Zn and Pb in dibasic lead phosphite extracts

Dibasic lead phosphite	[Zn] (mg/l)	[Pb] (mg/l)
Neutral extracts	5.69	3.44
Basic extracts	<0.05	<0.20
Acid extracts	111	242

Table 6
Concentration of Zn, P, and Al in zinc–aluminium phosphate extracts

Zinc–aluminium phosphate	[Zn] (mg/l)	[P] (mg/l)	[Al] (mg/l)
Neutral extracts	14.5	5.12	<0.12
Basic extracts	0.20	5.67	0.50
Acid extracts	155	44.2	0.177

Table 7
Concentration of Zn, P, and Mo in zinc phosphomolybdate extracts

Zinc phosphomolybdate	[Zn] (mg/l)	[P] (mg/l)	[Mo] (mg/l)
Neutral extracts	7.44	3.49	0.20
Basic extracts	0.43	9.70	0.15
Acid extracts	246	64.8	1.19

3.2. Inhibition power of extracts

As already described, samples of carbon steel were tested using the pigment extracts as electrolyte. Samples were exposed for 15 h to the extracts until they reached a stationary state. After this step, LP measurements were carried out. Figs. 1–6 show the LP curves obtained. As a reference, in each figure is included the LP curve in 3.5% NaCl solution recorded at the same pH condition for each sample studied.

In order to evaluate the activity of each system, the value of R_p was determined from the recorded LP curves (Table 9). The level of protection provided by the pigments has been assessed and compared using the above-defined %IP (Table 10).

Table 8
Concentration of Zn, P, and Fe in zinc–iron phosphate extracts

Zinc–iron phosphate	[Zn] (mg/l)	[P] (mg/l)	[Fe] (mg/l)
Neutral extracts	7.34	0.841	–
Basic extracts	<0.05	3.02	–
Acid extracts	110	29.7	0.20

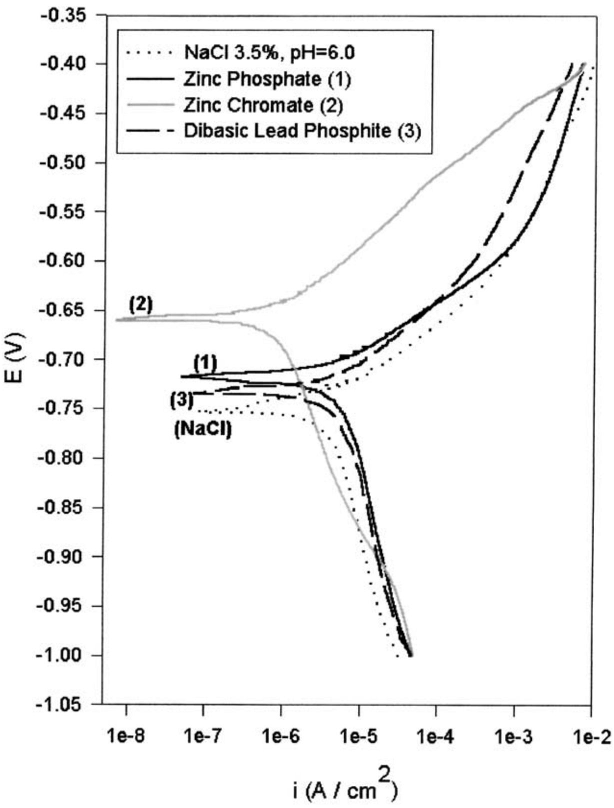

Fig. 1. LP curves obtained in neutral extracts of zinc chromate, zinc phosphate and dibasic lead phosphite.

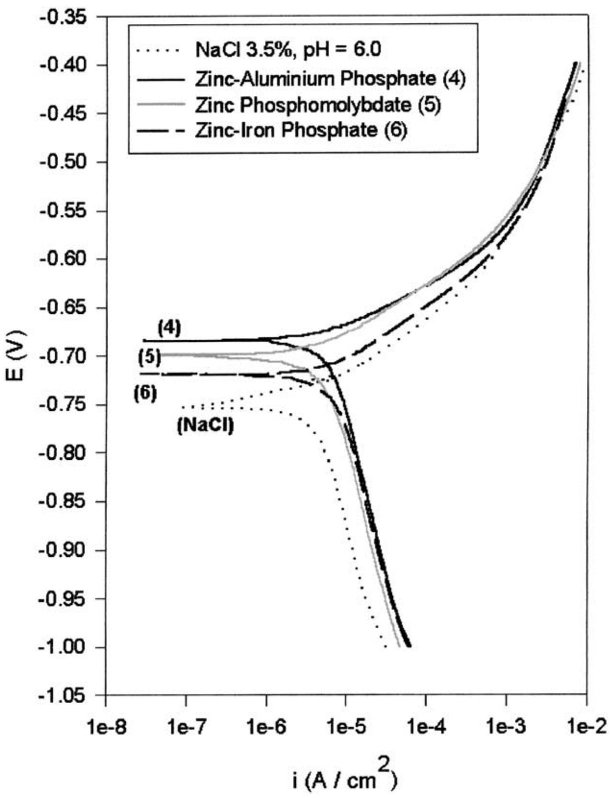

Fig. 2. LP curves obtained in neutral extracts of second-generation phosphates.

3.2.1. *Neutral extracts*

Fig. 1 plots the LP curves obtained in neutral extracts of zinc phosphate, zinc chromate and dibasic lead phosphite, while Fig. 2 plots the curves of second-generation phosphates, i.e., zinc–aluminium phosphate, zinc phosphomolybdate and zinc–iron phosphate. From theses curves, polarisation resistance values of carbon steel immersed in neutral extracts were calculated (Table 9). In this table, it can be observed that the neutral extract of zinc chromate produces a large increase in the polarisation resistance value. This finding can be related to a decrease in the steel corrosion rate. Thus, as can be observed in Table 10, zinc chromate can be considered as the pigment giving the most protection in neutral conditions (IP = 710%). Furthermore, when zinc chromate is used, an ennoblement in the corrosion potential of steel and a displacement leftward of the anodic branch in the polarisation curve are observed. Both effects are typical of anodic inhibitors, revealing that, when this pigment is used, the inhibitive effect must be related to the presence of chromate ions in solution. According to [30], chromate

Table 9
Polarisation resistance (R_p, Ω) of different extracts of pigments

	3.5% NaCl	Zinc phosphate	Zinc chromate	Dibasic lead phosphite	Zinc–aluminium phosphate	Zinc–iron phosphate	Zinc phosphomolybdate
Neutral extracts	3310	3616	26807	3942	3333	3295	3619
Basic extracts	2602	3715	5382	3403	2684	3173	3003
Acid extracts	3013	6480	1793	1828	5399	8736	6033

Table 10
Relative inhibition power (%) of different extracts of pigments

	Zinc phosphate	Zinc chromate	Dibasic lead phosphite	Zinc–aluminium phosphate	Zinc–iron phosphate	Zinc phosphomolybdate
Neutral extracts	9	710	19	1	0	9
Basic extracts	43	107	31	3	23	15
Acid extracts	115	−41	−39	79	190	100

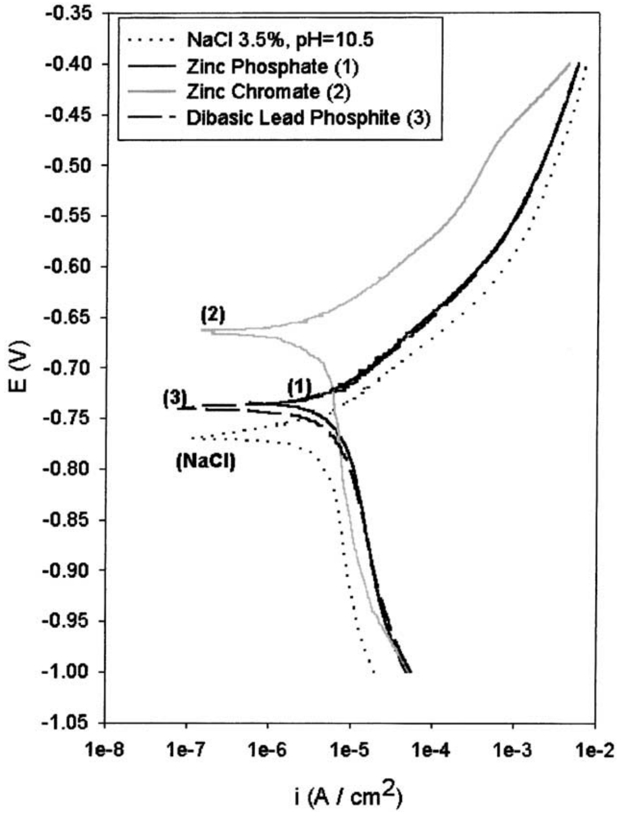

Fig. 3. LP curves obtained in basic extracts of zinc chromate, zinc phosphate and dibasic lead phosphite.

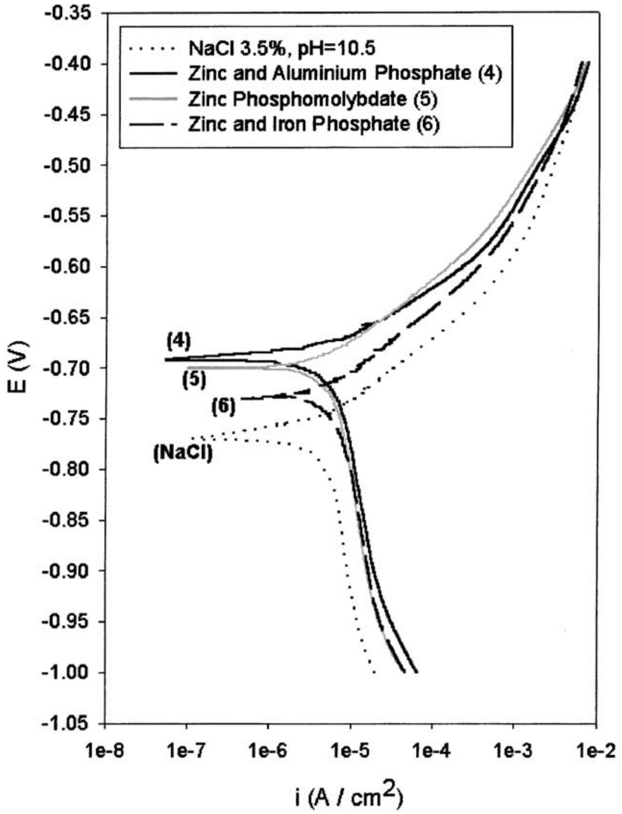

Fig. 4. LP curves obtained in basic extracts of second-generation phosphates.

ions promote the oxidation of Fe^{2+} to Fe^{3+} in anodic areas. As a consequence, Cr^{3+} and Fe^{3+} are produced and insoluble compounds are formed in anodic zones. These insoluble compounds form a passive layer that is responsible for the measured decrease of the corrosion rate.

LP curves obtained using the other neutral extracts investigated are close to that obtained for NaCl solution, although a small displacement of the curves can be observed in Figs. 1 and 2. Hence low values of %IP, Table 10, are estimated when neutral extracts of phosphate-based pigments are used.

The lower inhibition provided by neutral extracts of zinc phosphate, dibasic lead phosphite, zinc–aluminium phosphate, zinc phosphomolybdate and zinc–iron phosphate, in comparison with zinc chromate, can be explained analysing the data in Tables 3–8. As can be observed, the concentrations of Zn and P in neutral extracts are always below 15 and 6 mg/l, respectively. In contrast, the highest ion concentrations are measured in neutral extract of zinc chromate. In this solution the concentration of zinc and chromium are 92.4 and 92.0 mg/l, respectively. According to [31], in these conditions, practically all the dissolved Cr appears as chromate ions. Both the high concentration of dissolved ions and the better inhibitor properties of chromate can be considered as being responsible for the high level of protection observed.

3.2.2. *Alkaline extracts*

LP curves in alkaline extracts corresponding to the six pigments studied are plotted in Figs. 3 and 4. From these, it can be seen that the corrosion potential of carbon steel immersed in basic extract of the pigments is higher than when immersed in the solution without pigment (NaCl 3.5%, pH $= 10.5$). In alkaline media, basic extract of zinc chromate produces the largest displacement of the potential of carbon steel, with respect to that of the NaCl blank solution (Fig. 3). Less displacement of potential is observed when basic extracts of zinc phosphate, zinc chromate (in Fig. 3) and zinc–aluminium phosphate, zinc phosphomolybdate and zinc–iron phosphate (in Fig. 4) were employed. As with the neutral extract, zinc chromate shows the highest inhibition power of all the pigments tested (Table 10). However, as can be seen from the data in Table 10, the inhibition percentage of zinc chromate is much less in a basic medium than in a neutral medium. Thus, the basic extract of this pigment reached an IP of 107%, whereas the neutral extract of the same pigment reached an IP of 710%. These differences can be explained by considering the concentration of dissolved species in the two solutions. Data in Table 4 show that the Cr concentration is almost the same as that found in the neutral extract, i.e., 90 mg/l. However, the concentration of Zn in the basic extract is much lower than in neutral solution (3.4 mg/l vs 92.4 mg/l). The decrease in Zn concentration

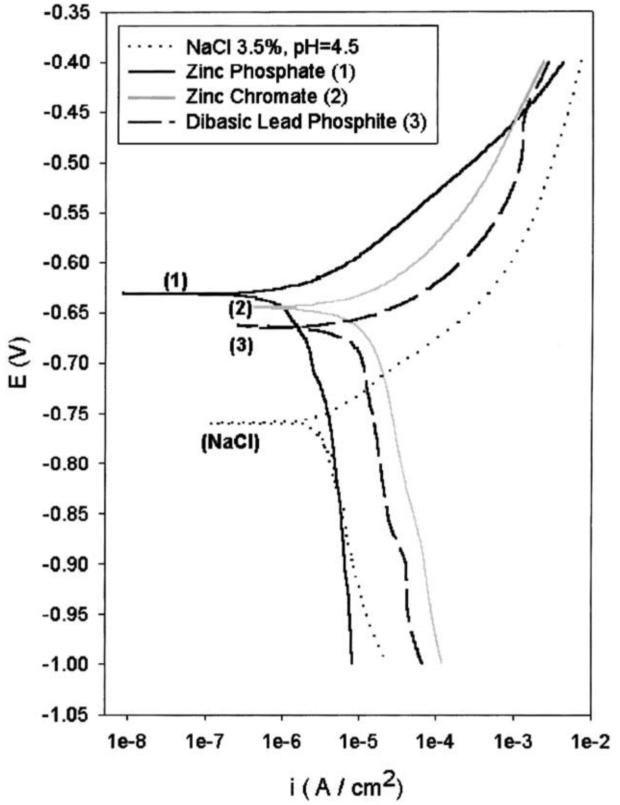

Fig. 5. LP curves obtained in acid extracts of zinc chromate, zinc phosphate and dibasic lead phosphite.

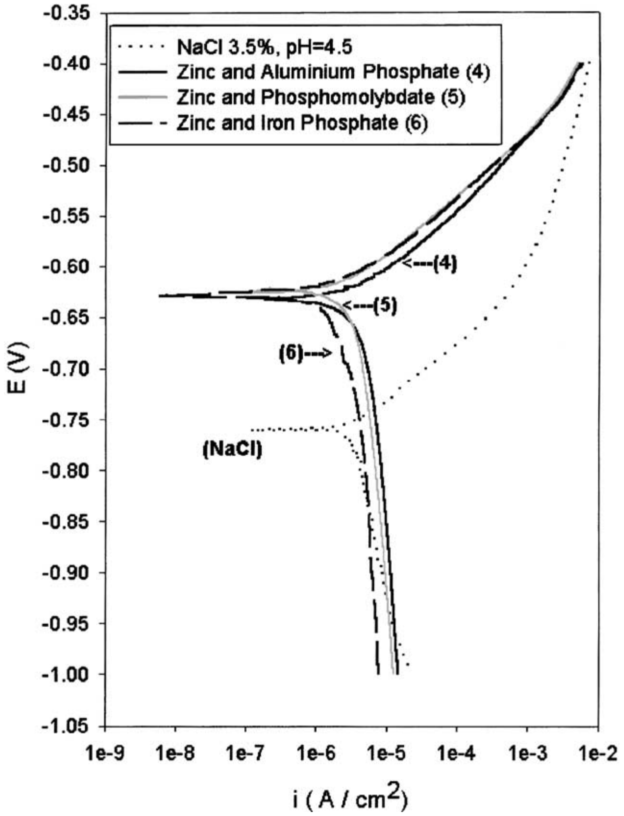

Fig. 6. LP curves obtained in acid extracts of second-generation phosphates.

in alkaline extract can be explained by the precipitation of $Zn(OH)_2$ during the extraction step. As Zn^{2+} ions act as cathodic inhibitors, the decrease in their concentration can cause the observed decrease in %IP in basic extract.

On the other hand, the other pigments studied present lower values of %IP, showing a similar behaviour to that observed for neutral extracts.

3.2.3. Acid extracts

LP curves of carbon steel in acid extracts of zinc chromate, zinc phosphate and dibasic lead phosphite are plotted in Fig. 5. From the direct observation of this figure, an ennoblement in corrosion potential can be observed similar to that found for neutral and basic extract. However, the most striking feature of the acid extracts is the calculated R_p values (Table 9). The R_p value for acid extract of zinc chromate is considerably lower than those calculated for neutral or basic solutions. This very reduced R_p value means that in acid extract zinc chromate does not produce any inhibition. This loss of inhibitor properties of zinc chromate acid extract may be related to the change in the actual nature of the dissolved ions. Data included in Table 4 show that, at the three pH values studied, zinc chromate extracts have a similar concentration of Cr. From the equilibrium constant values reported in [31], it can be concluded that in both neutral and basic extracts, Cr acts as CrO_4^{2-}, while $HCrO_4^-$ is the main specie present in acid extract. Further, according to [32], only the presence of CrO_4^{2-} causes the passivation of iron alloys and, significantly, an increase in the corrosive activity is reported in acid solutions [32].

In Table 9, it can also be observed that dibasic lead phosphite produces an increase in steel corrosion activity, leading to negative values of %IP in Table 10. In these experimental conditions, the low inhibition effect associated with ions generated by dibasic lead phosphite is compensated by the effect of Cl^- ions added in the acidification step. When acid extracts were made, it was necessary to add HCl to fix the pH at 4.5. Thus the concentration of Cl^- ions in acid extracts was higher than 3.5%. This activation effect of increasing the chloride concentration is revealed only when species that are poor inhibitors are present in the solutions.

Regarding zinc phosphate, R_p values included in Table 9 show reduced steel corrosion activity when this alternative pigment is used. Thus, contrary to the data reported for neutral and basic extracts, in acid solutions zinc phosphate shows higher %IP values than zinc chromate, i.e., 115% vs −41%. In Table 3, a high dependence of the solubility of zinc phosphate on the pH value can be observed. In acid extract [Zn] = 111 mg/l and [P] = 32.7 mg/l, whereas in basic extract their values are reduced to 5.69 and 1.22 mg/l, respectively. Thus the drastic changes in the inhibitor power of zinc phosphate solutions appears to be related to the dependence of its solubility on the pH level. Analysing the LP curves in Fig. 5, a combined cathodic and anodic inhibition mechanism may be proposed for zinc phosphate in acid extracts. According to [30], cathodic inhibition is related to the presence of Zn^{2+} ions, while anodic inhibition is due to PO_4^{3-} ions.

Fig. 6 plots the LP curves of carbon steel in acid extracts of zinc–aluminium phosphate, zinc phosphomolybdate and zinc–iron phosphate. These three pigments have a similar composition, in which the content of $Zn_3(PO_4)_2$ is much higher than that of Al, Mo or Fe. Data reported in Tables 6–8 show low concentrations of Al, Mo or Fe (0.177, 1.19 and 0.20 mg/l, respectively) in acid extracts as a consequence of the relatively small quantities of these elements in solid pigments. In contrast, high concentrations of Zn and P have been found in these acid extracts (Tables 6–8) (115, 246 and 110 mg/l of Zn, and 44.2, 64.8 and 29.7 mg/l of P have been found in extracts of zinc–aluminium phosphate, zinc phosphomolybdate and zinc–iron phosphate, respectively).

Taking into account that these pigments consist principally of $Zn_3(PO_4)_2$, the mechanism of action of these pigments in acid extract must be similar to that discussed for zinc phosphate pigment. LP curves in Figs. 5 and 6 show that the anodic branches are similar for these second-generation pigments and $Zn_3(PO_4)_2$. These results can be interpreted considering the anodic character of phosphate anions. However, some differences can be seen in the cathodic branches of the LP curves corresponding to these second-generation zinc phosphates. These differences could be related to the nature of the particular element used to modify the pigment (Al, Mo or Fe). Thus, in the LP curve of acid extract of zinc–aluminium phosphate, the cathodic current density is higher than in the other two zinc phosphate-based pigments. On the other hand, the lowest cathodic current density was measured when using zinc–iron phosphate acid extract as corrosive media. These values determine the inhibition power of the extracts; the lowest IP% corresponds to zinc–aluminium phosphate, whilst the highest value corresponds to the zinc and iron phosphate pigment (Table 10).

In conclusion, when acid conditions are employed, second-generation zinc phosphates show considerable improvement in inhibition property over zinc chromate, while avoiding its adverse environmental impact. Indeed, the toxicity of zinc phosphate-based pigments is 50 times lower than that of chromates [8], and zinc–iron phosphate presents an IP% value of 190%, against −41% shown by zinc chromate.

4. Conclusions

For six commercial pigments, the inhibitor properties against carbon steel corrosion in NaCl solutions have been studied; those tested were zinc phosphate, zinc chromate, dibasic lead phosphite, zinc and aluminium phosphate, ferrous and zinc phosphates and zinc phosphomolybdate. The last three of these are known as "second-generation" zinc phosphate-based pigments. In order to evaluate their inhibitive behaviour, neutral, basic and acid extracts of these pigments in NaCl at 3.5% were prepared. Then the extracts obtained were used as corrosive media of carbon steel.

ICP-AES analysis of the extracts has shown that the solubility of pigments increases inversely to pH. Thus, all the pigments studied have the highest solubility in acid extracts.

According to the results in neutral media, zinc chromate extract shows the highest inhibition power, which is attributed to the presence in solution of chromate ions, which provoke the oxidation reaction $Fe^{2+} \rightarrow Fe^{3+}$ in anodic areas. In consequence, a protective layer, incorporating Cr^{3+} and Fe^{3+}, develops in these zones on the metal surface.

When alkaline extracts are employed as corrosive media, zinc chromate shows the highest inhibition percentage. However, its inhibition level in basic conditions is lower than in neutral conditions.

The remaining pigments studied show low inhibition percentages both in neutral and basic conditions. These results have been related with the low solubility of the pigments in this pH range.

When acid medium is used, zinc phosphate and second-generation phosphates show higher inhibition percentages than zinc chromate, which actually presents a negative inhibition power. This leads to the conclusion that, in acidic media, zinc chromate increases the corrosion rate of the carbon steel studied.

Summarising, the obtained results suggest that the second-generation zinc phosphate pigments studied are more effective in acid media than zinc chromate. Moreover, the use of either zinc phosphate itself or the second-generation pigments based on zinc phosphates does not present the environmental risks associated with chromate-based pigments. Thus their use can be recommended in the formulation of primers to be applied to metals exposed to acidic environments.

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