

Influence of the composition of zinc-ethyl silicate paints on electrochemical properties

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The protection of steel by zinc-ethyl silicate primers is based on the general principle of cathodic protection by metallic zinc in contact with a ferrous substrate. The influence of the zinc content on the paint behaviour has been studied, but little attention has been paid to effects caused by the incorporation of additives, such as extender pigments, to the formulation.

The aim of this paper is to study the influence of the whole composition of zinc-ethyl silicate paints on their electrochemical properties. A second purpose is to establish the nature of the anticorrosive action of these paints. Four commercial zinc-ethyl silicate paints were chosen for these investigations.

It was found that the incorporation of extender pigments modified the behaviour of these paints. The anticorrosive action was due to the cathodic protection by zinc powder and the inhibition of the electrochemical reactions by corrosion products. The barrier effect, in the sense of ohmic resistance, provided by these paints was of lesser importance.

1. Introduction

The protection of steel by zinc-ethyl silicate primers is based on the general principle of cathodic protection by metallic zinc in contact with a ferrous substrate. It is necessary that the zinc particles in the dry film be packed closely enough to maintain electrical contact with one another and with the steel substrate. This allows the conduction of the electric current generated by the zinc-steel galvanic couple during the electrochemical reaction [1, 2].

When formulating a zinc-rich paint it is necessary to specify an adequate zinc content ensuring maximum particle packing in the dry film. Several studies have been carried out in order to elucidate the influence of the zinc content on the electrochemical properties of these paints. A zinc content higher than 60% by weight is recommended to achieve good protection [2–4].

Additives are incorporated in virtually all paint formulations. Little work has been done to clarify the influence of additives on the electrochemical properties of the paint film and its anticorrosive action.

Barite and agamaltollite were employed as extender pigments [5]. It was found that the presence of these pigments did not impair the anticorrosive performance of the paints. When the zinc content was low the extender pigment improved the behaviour of the paint.

This paper reports a study of the influence of the whole composition of zinc-ethyl silicate paints on their electrochemical properties. Four commercial paints, with very different composition, were

selected. They were analysed previously to determine the main components. Their electrochemical properties, corrosion potential, a.c. resistivity, polarization resistance, electrolytic zinc content and 'effective zinc' content were studied, taking into account, when necessary, the film thickness.

The second purpose of this paper was to establish the nature of the anticorrosive action of zinc-ethyl silicate paints.

2. Experimental details

2.1. Paint and panel preparation

The selected paints were two package products, one package containing the zinc powder and the other the vehicle and, in some cases, extender pigments. They were identified as P1, P2, P3 and P4.

The analysis of the binder was carried out according to the following steps:

- (i) Separation of the solid fraction by centrifugation to determine its percentage,
- (ii) Analysis of the solid fraction to determine its composition, solubility in organic solvents and the silica extractable by means of a hot (70 °C) 5% sodium hydroxide solution. The nature of the solids was determined by current analytical techniques [6] and by infrared spectroscopy,
- (iii) Determination of silica content in the liquid fraction by a gravimetric technique [6],
- (iv) Evaluation of zinc content in the dry film by a complexometric procedure [6, 11].

Table 1. Chemical analysis of the binder of four commercial zinc ethyl silicate paints (wt %)

Formulation	Solid fraction			Liquid fraction	
	Proportion in the mixture	Silica	Extenders in the solid fraction	Proportion in the mixture	Dissolved silica
P1	40	3.1	Ferric oxide 16 metallic silicates 70	60	20
P2	44	8.5	Clay 90	56	11
P3	14	7.3	—	86	23
P4	14	7.5	—	86	22

The results are displayed in Table 1.

Paints were prepared mixing zinc powder and binder, according to the manufacturers' instructions.

Test plates were prepared employing SAE 1010 steel, sandblasted to a 2.5 degree (SIS 05 59 00) specification and cleaned with toluene. Paints were applied by means of an adjustable film applicator. Final film thickness was measured by a magnetic gauge. A $70 \pm 5 \mu\text{m}$ dry film thickness was obtained.

2.2. Corrosion potential measurements

The cells to measure the corrosion potential across the paint film-steel substrate interface with respect to the silver-silver chloride electrode, were constructed by delimiting 2cm^2 circular zones on the painted surface and masking the remaining surface with a chlorinated rubber water resistant paint. An acrylic open cylindrical tube with one flat end, 7 cm long and 4 cm diameter, was then placed on the specimen and electrolyte placed in the tube. The measurements were carried out with a 701 A model Orion voltmeter.

The electrolytes were 1 M sodium perchlorate solution and 3% sodium chloride solution. Perchlorate ion is less aggressive than chloride ion.

The results for the sodium perchlorate solution are plotted in Fig. 1.

2.3. A.c. resistance and polarization resistance measurements

The a.c. resistance (at 1000 Hz) between the steel substrate and a platinum electrode, R_E , was also measured using a Phillips bridge. The cells were similar to those employed for corrosion potential measurements. The same electrolytes as for the corrosion potential measurements were employed. The resistivity as a function of the immersion time is plotted in Fig. 2 for 1 M sodium perchlorate solution.

The polarization resistance, R_p , for the four formulations was determined by a galvanostatic method [7-10]. The working electrode was a 1cm^2 painted specimen. The reference electrode was silver-silver chloride and a platinum counter electrode was chosen. Each painted specimen was polarized $\pm 50\text{mV}$ starting from the corrosion potential. The R_p value was determined from the slope of the i against E curve. The results are shown in Table 2.

2.4. 'Effective zinc' content

The 'effective zinc' content curve as a function of film thickness was obtained according to a procedure described previously [11]. The electrolytic zinc content (Fig. 3) was determined by passing 5 mA

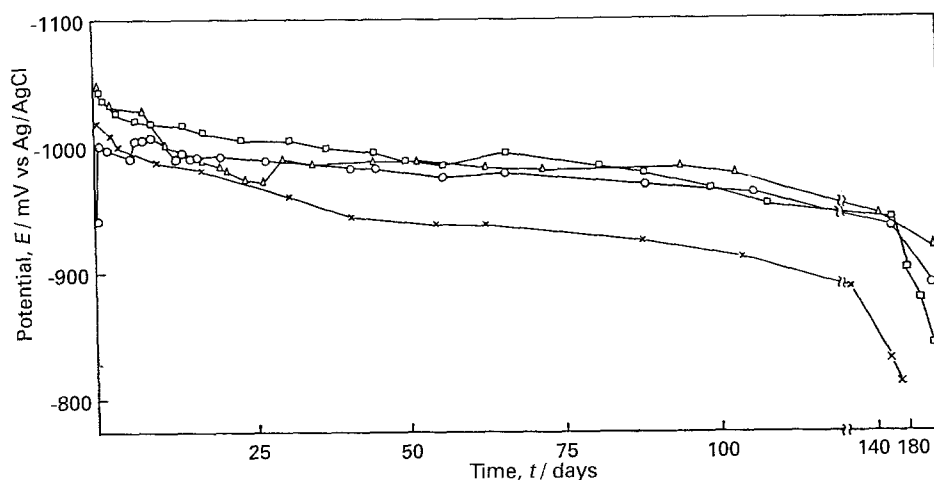


Fig. 1. The corrosion potential variation as a function of the immersion time against Ag/AgCl for the different formulations. Electrolyte: 1 M sodium perchlorate solution. Formulation: (x) P1, (Δ) P2, (\square) P3 and (\circ) P4.

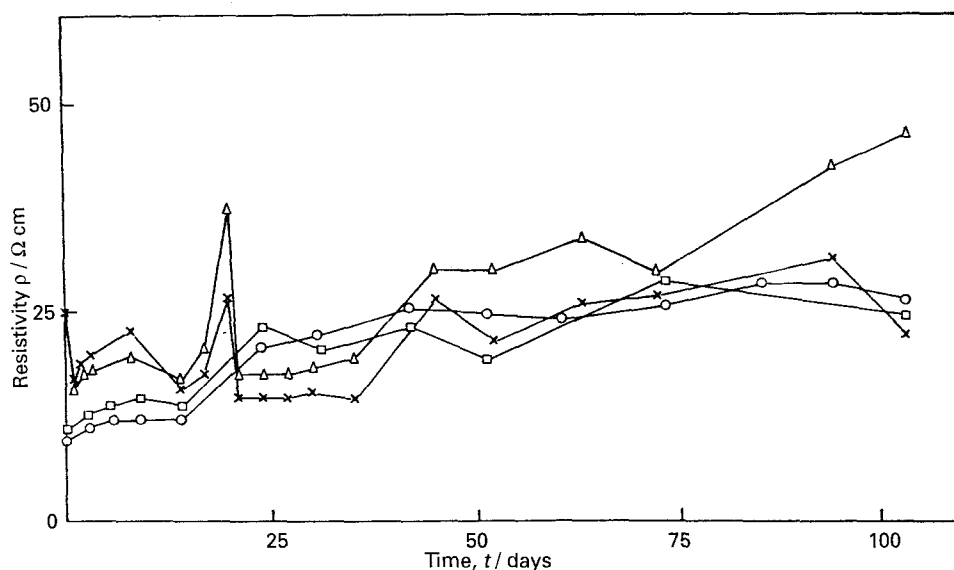


Fig. 2. Variation of the a.c. resistivity as a function of the immersion time for the different formulations. Electrolyte: 1 M sodium perchlorate solution. Formulation: (x) P1, (Δ) P2, (\square) P3 and (\circ) P4.

Table 2. Polarization resistance of SAE 1010 painted specimens for the different formulations and the zinc electrode as a function of the immersion time in 1 M NaClO₄ solution

Paint formulation	Cathodic $R_p/\Omega\text{ cm}^{-2}$		Anodic $R_p/\Omega\text{ cm}^{-2}$	
	1 day	10 days	1 day	10 days
P1	214	179	128	143
P2	86	446	71	321
P3	256	1286	92	1071
P4	75	554	68	536
Zn	427	750	183	607

current through a 1 cm² painted area, i.e. the time required for zinc particles to lose electrical contact. This end point was detected by a sudden change in the electrode potential (from -950 to +1100 mV vs SCE). The electrolyte was 1 M ammonium acetate (pH 8.2) solution. From this data and employing Faraday's law, the zinc able to conduct electrical current may be calculated. The total amount of zinc in the film was determined by a complexometric titration [6, 11]. The ratio electrolytic zinc/total zinc was called the 'effective zinc' content. The 'effective zinc' content for different formulations was plotted in Fig. 4.

The 'effective zinc' content decay curve as a function of the immersion time was also obtained

(Fig. 5). The panels were submerged in a 3% sodium chloride solution and the 'effective zinc' content determined for different immersion periods according to the above mentioned procedure [11]. The 3% sodium chloride solution was chosen because it is more aggressive than the sodium perchlorate solution. The film thickness of the painted panels was $70 \pm 5 \mu\text{m}$.

3. Results and discussions

3.1. Paints composition

Paints P1 and P2 had vehicles with similar percentages of solids and liquid. However, the percentage of soluble silica in the liquid phase was higher for paint P1. The composition of the solid fraction is quite different; P1 incorporated ferric oxide and metal silicates (potassium aluminium silicate and talc) and P2 a clay (China clay) as extender pigments.

The percentages of the solid and the liquid fraction in the vehicles P3 and P4 were similar. They did not incorporate extender pigments as P1 and P2. The silica content dissolved in the liquid fraction was also similar. The solubility of the solid fraction in toluene indicated the degree of hydrolysis of the binder. The higher the solubility, the less the hydrolysis degree. The P3 vehicle was less hydrolyzed than P4.

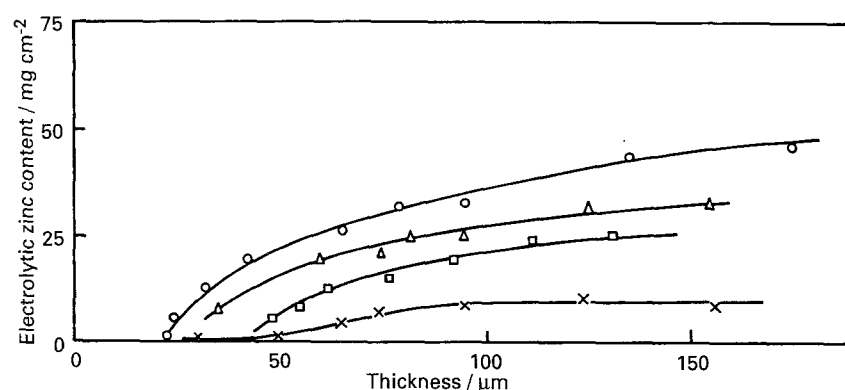


Fig. 3. The electrolytic zinc content by unit area as a function of the film thickness for the different formulations. Formulation: (x) P1, (Δ) P2, (\square) P3 and (\circ) P4.

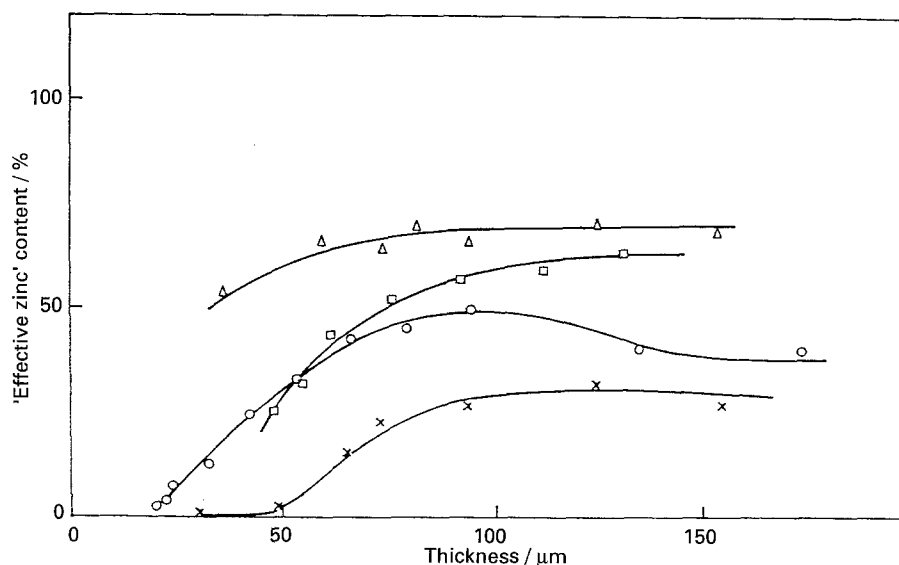


Fig. 4. 'Effective zinc' content percentage as a function of the film thickness for the different formulations. Formulation: (x) P1, (Δ) P2, (□) P3 and (○) P4.

The zinc powder/vehicle relationship suggested for P1, P2 and P3 was similar, 70/30 by weight, and 81/19 for P4.

The tested paints may be divided into two groups. One incorporated extender pigments (P1 and P2) and the other did not (P3 and P4). The zinc content in the dry film was 85% by weight on average, except for paint P4 which was 95%. Painted specimens with formulation P1, microscopically observed, showed a preferential settling of extenders with respect to zinc particles.

Painted specimens with formulation P2 showed excellent levelling properties and good finishing.

3.2. Corrosion potential measurements

The experimental results (Fig. 1) show that zinc-ethyl silicate paints do not fit the Wormwell and Brasher

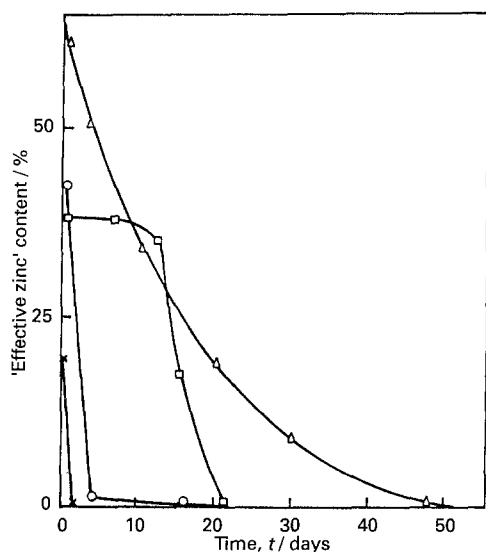


Fig. 5. 'Effective zinc' content variation as a function of the immersion time, for a given thickness, and for the different formulations. Electrolyte: 3% sodium chloride solution. Formulation: (x) P1, (Δ) P2, (□) P3 and (○) P4.

model [12–14], in the sense of exhibiting a slow rise (after an initial fall) towards more positive values during the first days of immersion. In the case of zinc-rich paints, the presence of zinc powder in the film shift the potential of steel in the negative direction and make it immune to corrosion.

The behaviour of zinc-ethyl silicate paints with respect to the corrosion potential variations must be interpreted as a continuous transition from the zinc corrosion potential ($E = -940$ mV vs Ag/AgCl in 1 M NaClO₄ solution) to the iron corrosion potential ($E = -650$ mV vs Ag/AgCl in 1 M NaClO₄ solution). The appearance of red iron oxide spots on the painted surface at potential values near to -900 mV was noted.

Three zones were distinguished in the corrosion potential against time curve (Fig. 1): (a) an initial shift towards more positive values during the first days; (b) a second zone where E remained almost constant with time for several months; and, (c) a rapid final decline of the corrosion potential which tended to match the iron corrosion potential. The behaviour of these systems was independent of the film thickness and depended on the composition of the paints (zinc content, extender pigments, etc.) and on the presence of paint film defects [3].

Paints showing the best performance had a more or less extended second zone and a relatively high (in terms of the absolute value) corrosion potential in this zone. This second zone is indicative of the paint quality. The more negative the potential values and the more extended the period comprised by this zone, the better its anticorrosive properties. During this period the ratio anode to cathode area changed continuously and zinc particles were covered with corrosion products and isolated from each other progressively. The protection afforded by the paint during this period could not be explained taking into account only the cathodic protection mechanism as some authors suggested [15].

The presence of extender pigments in the paint film influenced the behaviour of the paint with respect to the corrosion potential variations.

The paints with a high zinc content in the film and that with the clay as extender pigment showed the best behaviour. The incorporation of ferric oxide and metallic silicates to the paint proved to be detrimental. The behaviour in a 3% NaCl solution was similar, except that the second zone was 20% shorter, in time, than in 1 M NaClO₄ solution.

The electrode potential was more negative for the painted specimens than for metallic zinc. This suggests that metallic zinc in the paint was activated with respect to the zinc electrode alone. The activation of metallic zinc could be due to acid silanol groups present in the surface of the silica matrix. This has also been observed through impedance measurements [5].

3.3. A.c. resistance and polarization resistance measurements

The a.c. resistance showed a final value which was slightly higher than the initial one. Substantial differences were not observed among the different formulations, except for formulation P2. The incorporation of clay in the paint produced better results, increasing the resistance, at long time exposures, by a factor of two with respect to other formulations (Fig. 2).

The low resistance values observed for these formulations led to the conclusion that corrosion products did not form a high ohmic resistance insulating barrier which would protect the metal surface as suggested in the literature [1-3]. However, oxygen transport and ion diffusion through this layer could be partially inhibited [16]. A barrier effect in the sense of ohmic resistance is achieved when the film has a resistance higher than 10⁴-10⁵ Ω. In that case the corrosion rate of steel is not measurable. Classical insulating polymeric films exhibit resistance values higher than 10⁸ Ω.

The resistance values were low, but were higher than the specific conductivity of the 1 M sodium perchlorate solution (15 Ω cm). This fact suggested that a partial blocking of the metal surface occurred [16].

3.4. Polarization resistance measurements

The experimental values found for R_p (Table 2) showed that after one day immersion the values were relatively low and the value for zinc metal was higher than those found for the paints. After a 10 day period, when corrosion products appeared on the painted specimens, the R_p values for the paints increased and in some cases greatly exceeded the value corresponding to metallic zinc. Since R_p values are higher than those of R_E (the a.c. resistance), it must be concluded that the inhibition of both anodic and cathodic reactions is responsible for the protection afforded by these paints when corrosion products appear on the painted surface [16]. The

cathodic reaction being slightly more polarized than the anodic one. The corrosion products were mainly zinc hydroxide with silica [17].

The incorporation of ferric oxide and metallic silicates to the paint produced a detrimental effect, lowering the polarization resistance. The paint prepared employing the vehicle P3, which contained ethyl silicate with the lower degree of hydrolysis showed the higher polarization resistance.

3.5. 'Effective zinc' content

Although the total amount of zinc in the paint film increases linearly with film thickness, Fig. 3 shows that the 'electrolytic zinc content' does not increase in the same way. This caused the 'effective zinc content' not to increase as the film thickness increased (Fig. 4). In this investigation, the paint with a high zinc content in the paint film did not show the highest 'effective zinc' content (Fig. 4). The formulation which contained clay showed the best performance and that with ferric oxide and metal silicates as extender pigment the worst.

The 'effective zinc' content decreased significantly with immersion time. The current passing through the paint film caused a premature disbondment of the film. From data plotted in Fig. 5 it may be seen that most formulations failed in keeping electrical contact between the film and the substrate, except that containing China clay. The incorporation of clay to the paint film proved to be very effective because it extended the duration of the cathodic protection.

4. Conclusions

The following points can now be made:

- (i) The zinc powder content, the presence of extender pigments and the nature of the binder influence the electrochemical properties of the paints.
- (ii) The low resistance values clearly show that there is not an ohmic barrier effect but a partial blocking of the surface must be occurring.
- (iii) Initially, the steel substrate is protected cathodically by zinc powder. When corrosion products appear on the metallic surface the cathodic (oxygen reduction) and the anodic (zinc oxidation) reactions become partially inhibited.

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